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THE POST-MORTEM IMBIBITION OF ARSENIC.

BY FRANK S. SUTTON.

There is ample evidence that when arsenious oxide is introduced into the *living* organism it is absorbed and distributed, through the medium of the circulation, to all the tissues and organs of the body, and after death it may readily be recovered from any of these by appropriate chemical processes. It was thought, until very recently, that upon this fact rested a certain means of distinguishing between ante-mortem poisoning by arsenic and its introduction into the body after death, either for preservative purposes, or from motives less innocent; it being presumed in the latter instance that diffusion to the viscera outside of the alimentary canal would be prevented by the prompt conversion of any dissolved arsenic into insoluble sulphide by the gases of decomposition. This view is partly sustained by the undoubted fact that whenever arsenious oxide is thrown into the stomach or rectum of a dead body, the viscera in the immediate neighborhood are shortly found to be stained in varying degrees of intensity by yellow arsenic sulphide, and it is hence easy to account for the conviction long held by toxicologists that the presence of arsenic in the *viscera* of the body is proof of its ante-mortem administration. It remains to be seen, however, whether by subsequent oxidation of this sulphide to arsenic acid, or by solution in the ammoniacal liquids which decomposing nitrogeneous matters are so apt to give

rise to, the means for extensive diffusion might not ultimately prevail.

Orfila was the first to give the subject scientific investigation, the results of his experiments being announced as early as 1839. These experiments, which consisted in post-mortem injections of arsenious oxide per mouth and rectum, both of the dog and the human subject,[1] demonstrated that in from one to three weeks, extensive diffusion to the viscera of the abdomen invariably occurred, and at numerous other places in the same work the author speaks of having established beyond doubt the fact of post-mortem diffusion to "all the organs of the body." It is to be noted, however, that nowhere, so far as the writer is aware, is the specific statement made that arsenic was either sought for or recovered from the *brain.* These early experiments of Orfila do not appear to have taken very strong hold among toxicologists, for the impression soon became current that the presence of arsenic in the *viscera* is demonstrative evidence of its introduction into the system during life, and it is only within a very recent period that this idea, so tenaciously held on to, has been forced out of sight.

In a paper read before the College of Physicians of Philadelphia, November 1, 1876, on the "Post-Mortem Imbibition of Poisons," Dr. Jno. J. Reese embodies a brief account of some experiments on this subject by Dr. Geo. Y. McCracken, as recorded in an inaugural thesis, presented to the Auxiliary Faculty of Medicine, University of Pennsylvania, June, 1876. The experiments with arsenic consisted in post-mortem injections into the stomachs of three dogs, and after burial for the respective periods of 21, 44 and 59 days, the principal viscera of the abdomen are stated to have contained arsenic, but the presence of the poison does not seem to have been looked for either in the viscera of the thorax or in the brain. The steps of the analytical process are not mentioned.

At a recent murder trial[2] in Michigan, the body of a lady who had died with symptoms of arsenical poisoning was exhumed 105 days after death, and, upon chemical analysis, Prof. Prescott found about 20 grains of arsenious oxide in the stomach and rectum together, and a small amount was also recovered from the liver; at a subsequent period the body was again disinterred and the brain examined for arsenic, but none seems to have been found.

[1] Traité de Toxicologie, Vol. I, p. 384, 5th edition.
[2] Jour Amer. Med. Assoc., Aug. 4, 1883.

It being alleged at the trial that the husband had thrown arsenic to the amount of perhaps a teaspoonful into the mouth and rectum after death in order to preserve the body for removal, this fact gave rise to the query, "Granting that the arsenic was injected into the mouth and rectum in the manner claimed, could it reach the liver and other organs outside the alimentary canal?" Upon this question the experts were equally divided, and in order to throw some light upon it, Drs. Vaughan and Dawson undertook a couple of experiments, one upon a musk-rat, the other upon the cadaver. In both instances, after injection per mouth and rectum with arsenious oxide suspended in water, and burial for 25 days, chemical analysis revealed arsenic in nearly all the organs of the body, and in both cases arsenic was found in the *brain*. Commenting upon the comparatively large amount found in the brain of the musk-rat, the authors state that in the animal the bones of the skull are thin and not very firmly united; and similarly, seeking an explanation of its presence in the brain of the human subject, the suggestion is offered that possibly owing to a regurgitation into the pharynx and nose, noticed during the process of injection, some of the arsenic adhered to the roofs of the passages and thence diffused into the cavity of the skull.

The chemicals used in the foregoing analyses are stated to have been proved free from arsenic. The analytical method adopted consisted in destroying the tissues by potassium chlorate and hydrochloric acid, and from the ultimate product metallic mirrors were subsequently obtained by the modified Marsh apparatus of Chittenden and Donaldson.

In the same communication the authors embody the results of an experiment by Prof. Kedzie, of the Michigan Agricultural College, demonstrating diffusion of arsenic in the body of a cat, but no attempt seems to have been made to recover the poison from other than some of the abdominal and thoracic viscera.

Consideration of the foregoing experiments, which seem to be the only ones upon this subject of which there is any published record, leaves no room for doubt of the wide distribution of arsenic to the organs of the abdomen and thorax by cadaveric imbibition, both in the lower animals and in man, though we may question whether its presence in the heart and lungs is not to be accounted for on the assumption that part of the rejected fluid passed down the trachea. The evidence of its diffusion to the brain is much less

satisfactory, as upon this aspect of the case Orfila is silent, while the only other testimony is conflicting. In the case of the human body examined by Prof. Prescott, 105 days after the alleged introduction of the arsenic, none seemed to have found its way into the contents of the skull, though the abdominal organs contained an abundance; on the other hand, in the experiments of Drs. Vaughan and Dawson, where in both instances the time for diffusion was much shorter, the brain is stated to have contained appreciable quantities. This disparity, coupled with the fact that the affirmative testimony is somewhat weakened on account of the thin loose-jointed character of the bones of the skull in the musk-rat, and the regurgitation into the pharynx and nose in the case of the cadaver, serves to render the evidence of diffusion to the *brain* less positive and convincing than the importance of the subject in its medico-legal aspects would seem to demand. In the paper by Dr. Reese, already referred to, the author remarks that should it be proved as alleged by Scolosuboff, of Moscow,[1] that arsenic is deposited during life in the brain and cord, "we shall be in possession of a positive and unequivocal chemical method of distinguishing between ante-mortem and post-mortem poisoning by arsenic (and probably by other metals), by the detection of the poison in the brain and spinal cord, since it is scarcely conceivable that a poison introduced into a body after death could penetrate by imbibition within the cavity of the cranium or spinal column."

In view of these facts the following experiments were particularly directed towards determining the question of diffusion into the brain, and at the same time it was hoped to establish more definitely the shortest period during which general diffusion may be expected to take place. The subjects of these experiments were mongrel dogs, seven in number, as nearly uniform in weight as circumstances permitted. Death was produced by chloroforming, and in cases except where the conditions of the experiment called for a deviation, the aim was to inject 24 hours after death. The bodies were injected per mouth and rectum in accordance with the following uniform plan. The glottis being closed by a finger in order to avoid getting into the trachea, a straight glass tube was passed down the œsophagus into the stomach, and by means of a funnel attachment, 3 grams of arsenious oxide, diffused in about 50 cc. of water, were thus intro-

[1] Archives de Physiologie, No. 5, Août et Septembre, 1875.

duced. The same tube then sufficed to convey a like amount into the rectum, previously cleared as far as possible of its fæcal contents, but not more than 10 cc. of water were here found advisable, owing to the tendency to escape from the bowel. Thus injected, the bodies were buried under about 50 centimetres of soft earth for periods varying from 3 days to 3½ months, and then taken up for the removal of liver, kidneys and brain, and in one instance part of the spinal cord. Great care was taken to avoid contaminating any organ through the instruments used in removing preceding ones, and in no case was the alimentary canal cut into until all the desired viscera had been excised. In the experiments numbered V, VI and VII, where the periods of diffusion were shortest, and consequently the chances of arsenic reaching the brain at a minimum, the cranium was opened first, and its contents removed before cutting into the abdomen, so as to guard as fully as possible against accidental transfer from the one region to the other; and throughout the entire analysis each brain was examined in a separate fume closet, in order to still further avoid the possibility of contamination by extraneous sources.

The method of analysis was that recommended by Prof. Theo. G. Wormley[1] and in use at the laboratories of the Med. Dept., Univ. of Penna. Briefly, it consists in breaking up the tissues by potassium chlorate and hydrochloric acid, reduction by solution of sulphurous acid to condition of lower oxide, precipitation by a washed stream of sulphuretted hydrogen, solution of the precipitate in weak ammonia water, evaporation to dryness, repeated oxidation by strong nitric acid, followed by the addition of a few drops of strong solution of caustic potash with re-evaporation to dryness, and finally thorough charring by an excess of pure sulphuric acid; the latter is then completely expelled by heat, the pulverised carbonaceous mass extracted with acidulated water, and from the perfectly *colorless* filtrate the arsenic may be at once thrown down as magnesium ammonium arseniate, by rendering alkaline and adding magnesia mixture, or may be transferred to the Marsh apparatus; for Reinsch's test reduction by sulphurous acid is, of course, essential.

The purity of the reagents used in the foregoing process was proved for each in detail by Reinsch's test, excepting only the nitric acid, and collectively by the Marsh apparatus, by means of

[1] Micro-chemistry of Poisons, 2d edition, p. 301 *et seq.*

a blank experiment. Corroborative evidence of purity is also furnished by the fact that in Experiment No. VII the kidneys gave no trace of mirror whatever. It should be added that in those cases where Reinsch's test was employed, the presence of octahedral crystals was always demonstrated by the microscope. The only quantitative determination made was in the case of the liver of the dog longest buried, it being presumed from its size and position that this organ would contain the largest amount of arsenic, and the more in proportion as exposure to the influence of diffusion was protracted. In all cases the entire organs were used for the analysis. Following are the results in detail of the several experiments.

Experiment I.

Weight of dog, five and a half kilos; arsenic injected January 8, 1883, 23 hours after death; exhumed April 19, 1883. Length of interment, 102 days.

Post-Mortem Appearances.

Internal organs in good condition, appearing firm and natural, but brain very soft; a few dull yellow spots seen at sundry parts of the intestines; stomach half filled with a grayish pulp, but no yellow patches seen upon its walls.

The Liver.—Weight, 161 grams. One-fifth part of the final solution, representing one-fifth of the entire amount of arsenic recovered, easily responded to Reinsch's test, giving an abundant deposit on copper which was readily volatilised and condensed in octahedra. The arsenic in the remaining four-fifths was precipitated as magnesium ammonium arseniate, dried at 100° (C.) on an equipoised filter, and found to weigh 0.0153 gram. The whole amount recovered, then, was 0.019 gram, equivalent to 0.0099 gram arsenious oxide.

The Kidneys.—Weight = 42 grams. *One-tenth* part of the final solution gave prompt response, with octahedra, under Reinsch's test.

The Brain.—Weight = 51 grams. *One-fifth* part of the final solution tested with copper foil gave a perceptible steel gray coating from which octahedra were easily obtained. Verified by Marsh's test with part of the remaining four-fifths.

EXPERIMENT II.

Weight of dog, 5.2 kilos; arsenic injected February 5, 1883, twenty-six hours and a half after death; exhumed April 19, 1883. Length of interment, 74 days.

Post-Mortem Appearances.

Internal organs in good condition; bright yellow patches of various parts of intestines; stomach congested and showing one or two small yellow spots; empty, excepting a small bunch of grass.

The Liver.—Weight, 191 grams. *One-tenth* part of the final solution readily responded to Reinsch's test with production of octahedra.

The Kidneys.—Weight, 41 grams. *One-tenth* part of the final solution promptly coated copper from which octahedra were easily obtained.

The Brain.—Weight, 59 grams. *One-fifth* part of the final solution gave a good deposit on copper, and the resulting octahedra were readily made out. Verified presence of arsenic by Marsh's test.

EXPERIMENT III.

Weight of dog, 10.2 kilos; injected arsenic March 6, 1883, twenty-four and a half hours after death; exhumed April 19, 1883. Length of interment, 44 days.

Post-Mortem Appearances.

Internal organs well preserved; abundant yellow patches on rectum, colon and upper small intestines; stomach filled with food, congested in places, and with bright yellow spots on its anterior surface.

The Liver.—Weight, 300 grams. *One-tenth* part of the final solution gave heavy deposit on copper with subsequent octahedra.

The Kidneys.—Weight, 75 grams. *One-tenth* part of the final solution gave good deposit under Reinsch's test, but not so ready in coming down as in the liver solution.

The Brain.—Weight, 65 grams. *One-fifth* part of the final solution deposited on copper with difficulty and not very heavily;

yielded an invisible sublimate which showed under the microscope merely as opaque dots. Presence of arsenic verified by Marsh's test.

EXPERIMENT IV.

Weight of dog, five and a half kilos; arsenic injected April 1, 1883, 25 hours after death; exhumed April 19, 1883. Length of interment, 18 days.

Post-Mortem Appearances.

Some dull yellow patches in rectum, and a faint yellow tint in parts of the small intestine; stomach congested and empty, a few yellow spots on its greater curvature.

The Liver.—Weight, 230 grams. *One-tenth* part of the final solution promptly responded to Reinsch's test, octahedra being readily obtained.

The Kidneys.—Weight, 48 grams. *One-tenth* part of the final solution gave a less ready deposit than the liver solution; octahedra easily recognised.

The Brain.—Weight, 41 grams. *One-fifth* part of the final solution tarnished copper only when nearly evaporated to dryness; the sublimate, as in the case of the brain in the previous experiment, was not visible to the naked eye, and showed under the microscope merely as a collection of opaque dots. Presence of arsenic verified in the remainder by Marsh's test.

EXPERIMENT V.

Weight of dog, about 12 kilos; arsenic injected May 7, 1883, 6 hours after death, the body being quite cold; exhumed May 17, 1883; length of interment, 10 days.

Post-Mortem Appearances.

Abundant bright yellow patches in rectum and colon, the most vivid yet seen; omentum also yellowish in places; stomach almost empty, containing only a small amount of greenish liquid and a little grass; deeply congested, as also the upper part of the duodenum.

The Liver.—Weight, 417 grams. One-tenth part of the final solution gave the usual prompt response to Reinsch's test, octahedra being readily recognised.

The Kidneys.—Weight, 85 grams. One-tenth part of the final solution gave results similar to those of the corresponding liver solution.

The Brain.—Weight, 72 grams. Concentrated the *whole* of the final solution to a few cubic centimetres, and upon adding to a Marsh apparatus, a small but dense mirror speedily appeared.

Experiment VI.

Weight of dog, about 7 kilos; arsenic injected May 26, 1883, about 10 minutes after death, as near as could be determined; exhumed at the expiration of 3 days.

Post-Mortem Appearances.

Some few yellow spots in small intestines and parts of omentum; deep congestion of stomach, duodenum and liver; stomach empty; corrugations at cardiac end overlaid by an abundant collection of arsenious oxide; beneath this deposit appeared a few yellow specks.

The Liver.—Weight, 187 grams. One-tenth part of the final solution gave dense mirror in the Marsh apparatus.

The Kidneys.—Weight, 47 grams. One-tenth part of the final solution likewise gave a heavy mirror in Marsh's apparatus.

The Brain.—Weight, 63 grams. Concentrated final solution to about 1 cc. and upon throwing into a Marsh apparatus a small deposit shortly appeared, which was somewhat increased after 20 minutes, but which never amounted to more than a well-marked *stain.*

Experiment VII.

Weight of dog, 4½ kilos; arsenic injected June 2, 1883, 24 hours after death; exhumed at end of 3 days. In addition to the usual viscera, about 3 inches of the spinal cord were removed by sawing through the vertebral laminae in the middle dorsal region.

Post-Mortem Appearances.

Intensely yellow patches, by far the most vivid and abundant of any in the entire series, were noticeable in the region of the lower colon and rectum; stomach very full, most of the mass appearing

to be hair; congested at cardiac end, and in the same region were found deep yellow spots on the mucous membrane. A lump of hardened fæces was noticed not far above the rectum, and lodged against it was a mass of arsenious oxide.

The Liver.—Weight, 147 grams. One-sixth part of the final solution gave a dense mirror in the Marsh apparatus; the remaining five-sixths, reduced by sulphurous acid and subjected to Reinsch's test, coated but three small slips of copper, the arsenic then becoming exhausted.

The Kidneys.—Weight, 35 grams. The *whole* of the final solution, concentrated to a small bulk and thrown into Marsh's apparatus, gave no deposit whatever even after an interval of 15 minutes. This unlooked-for result may perhaps be explained by the presence of the impacted fæces in the lower bowel, already referred to, preventing ascent of the arsenic far enough up the intestine to reach the kidney in the short time allowed for diffusion, though it is not easy to understand why some should not have worked its way down from the stomach. Possibly position during burial, inclining the stomach in this or that direction, may have exerted an influence.

The Spinal Cord.—Weight, 3 grams. The final solution, concentrated to a small bulk and thrown into a Marsh apparatus, gave a faint deposit not perceptibly increased at the end of 15 minutes; considering the small part tested, it is likely that the entire cord would have produced a distinct mirror.

The Brain.—Weight, 42 grams. Upon concentrating the final solution to a few drops and pouring into the Marsh apparatus, a barely visible *ring* shortly appeared, which did not seem to increase materially during the succeeding 15 or 20 minutes. This was the faintest deposit of the entire series.

The foregoing results may be tabulated as follows:

	I.	II.	III.	IV.	V.	VI.	VII.
Weight of Dog.	5½ kilos.	5.2 kilos.	10 2 kilos.	5½ kilos.	12 kilos.	7 kilos.	4½ kilos.
Time of Injection.	23 hrs. after death.	26½ hrs. after death.	24½ hrs. after death.	25 hrs. after death.	6 hrs. after death.	10 mins. after death.	24 hrs. after death.
Condition of Stomach.	Half-full of grayish pulp	Empty, except a little grass.	Filled with food.	Empty.	Almost empty; greenish liquid, and small bunch grass.	Empty.	Filled mainly with hair.
Length of Interment.	102 days.	74 days.	44 days.	18 days.	10 d ys.	3 days.	3 days.
Liver.	Contained .0999 gram arsenious oxide; precip. and weighed as Mag. Arseniate.	One-tenth final sol. promptly responded to Reinsch's test, giving octahedra.	One-tenth final sol. yielded heavy deposit on copper; octahedra easily obtained.	One-tenth final sol. readily gave octahedra under Reinsch's test.	One-tenth final sol. gave usual prompt response with octahedra, under Reinsch's test.	One-tenth final sol. gave dense mirror in the Marsh apparatus.	One-sixth final sol. gave dense mirror in the Marsh app.; remaining five-sixths under Reinsch's test coated but 3 slips of copper.
Kidneys.	One-tenth final sol. readily gave octahedra under Reinsch's test.	One-tenth final sol. under Reinsch's test, promptly gave octahedra.	One-tenth final sol. gave good deposit with octahedra, but not so ready in coming down as the corresponding liver solution.	One-tenth final sol. gave less ready deposit than the above liver solution; octahedra easily made out.	One-tenth final sol. gave good deposit; sublimate showed octahedra.	One-tenth final sol. gave a heavy mirror in Marsh's apparatus.	Final sol. concentrated and thrown into Marsh's app. gave no mirror after 15 mins.; arsenic absent.
Brain.	One-fifth final sol. gave octahedra under Reinsch's test; verified by Marsh's apparatus.	One-fifth final sol. responded to Reinsch's test, giving octahedra; verified by the Marsh apparatus.	One-fifth final sol. deposited with difficulty; sublimate invisible; appeared as minute opaque dots under the microscope; verified by Marsh's test.	One-fifth final sol. tarnished copper only when nearly evaporated to dryness; sublimate invisible, but shows under microscope as opaque spots, verified by the Marsh apparatus.	Final sol. concentrated to a few cc. gave a small but dense mirror in the Marsh apparatus.	Final sol. concentrated to 1 cc. gave a well marked *stain* in the Marsh apparatus, but no mirror.	Final sol. concentrated to a few drops produced a barely perceptible ring in the Marsh apparatus; faintest of the entire series.
Spinal Cord.							Final sol. concentrated to small bulk, gave faint deposit in the Marsh apparatus; only 3 ins. of cord were used in this experiment.

On examining these results it will be noticed that while the brain of the dog buried ten days contained sufficient arsenic to give a small dense *mirror* in the Marsh apparatus, that from the brain of the dog buried three days, and in which the injection took place ten *minutes* after death, merely produced a well-marked *stain*, and, finally, in the brain of the dog buried three days but which had been injected 24 hours after death, the arsenic was present only in sufficient quantity to appear as an almost imperceptible *ring*. This successive gradation of intensity, occurring just as might be expected under the conditions of experimentation, granting that diffusion takes place at all, tends strongly towards showing that the presence of arsenic in the brain in these cases was not accidental, and that the amount contained, other things being equal, bears a direct ratio to the length of time for which diffusion was permitted to act. The experiment of injecting the poison shortly after death was undertaken in order to determine whether the greater fluidity and warmth of the parts would not favor a more rapid diffusion, and from the fact that a larger amount of arsenic was recovered from the brain in this case than in the experiment where the dog was injected 24 hours after death, the length of burial being the same in both cases, the question would seem to be answered in the affirmative.

It is of interest to know by what route the arsenic reached the brain, but the facts at command do not warrant a definite conclusion. It is not very likely that in so short a period as three days general diffusion through the tissues and entrance into the cranium through the foramen magnum would have taken place, but there are two or three other avenues worthy of attention which are more promising. The intestines being richly supplied with lymphatics, all leading to the thoracic duct, and this in turn emptying into the subclavian vein at the base of the neck, a possible route here suggests itself; a more roundabout way would be through the portal system to the heart and thence up the superior vena cava; at autopsies and in the dissecting-room we generally find the blood in the veins more or less fluid, doubtless through the breaking down of the primary coagulum, and thus the routes here sketched are among the possibilities. On the other hand, the presence of arsenic in the spinal cord, as evidenced in Experiment VII, and which in fact was there sought with no other object than to locate the channel through which the arsenic reached the brain, affords

good grounds for the belief that part, at least, finds access to the cranial cavity through the medium of its continuation in the spinal column. It will be remembered that the sub-arachnoid space is filled with fluid, continuous with a similar fluid in the brain, and thus, having diffused through the tissues about the vertebral column and reached this space, an easy channel to the brain is afforded.

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A METHOD OF FILTRATION BY MEANS OF EASILY SOLUBLE AND EASILY VOLATILE FILTERS.

BY F. A. GOOCH.

The processes of analysis, in which it is desirable to redissolve precipitates from the filter after washing, or to separate a mixed precipitate into parts by the action of appropriate solvents, are many.

When a complete solution is the object, and the precipitate yields easily to solvents which do not affect paper injuriously, the use of the ordinary filter offers no difficulty. When, however, precipitates are to be treated with reagents which disintegrate paper filters, the case is otherwise; and the attempt to remove, by solvents, any individual part of a mixed heterogeneous mass upon a filter is always an uncertain matter. As examples of cases of this sort, difficult to deal with, we may take the solution of acid sodic titanate in strong hydrochloric acid; or the purification of baric sulphate from included salts by digestion in strong hydrochloric acid; or the separation of sulphides which are soluble from those which are insoluble in alkaline sulphides; or the washing out of free sulphur from precipitated sulphides by means of carbon disulphide; or the separation of calcic and baric sulphates by the action of sodium hyposulphite. In cases of this nature it is often convenient to make use of the asbestos filter which I have previously described;[1] but this sometimes has its

[1] This Journal 1, 237.

disadvantages. Thus, to recur to the examples just cited, acid sodium titanate may be filtered and washed upon an asbestos filter, and felt and precipitate treated together with hydrochloric acid, but it will be impossible to determine when solution is effected because of the floating asbestos; and in separating the sulphides it would be necessary to know the weight of the asbestos felt, since it must be weighed finally with the insoluble sulphides, unless removed by a special treatment which involves the solution, filtration and reprecipitation of the latter.

It is to meet cases like these that I have sought a filter which, in the reversal of the ordinary mode of separating filter and precipitate, should dissolve easily in solvents which do not affect the ordinary precipitates met with in analysis. The material which seems best suited to the case—light and fluffy, capable of making secure filters of any desirable degree of porosity, sufficiently insoluble in water and aqueous solution of salts, alkalies and acids (excepting strong sulphuric, strong nitric, and glacial acetic acids), easily soluble in naphtha, benzol, carbon disulphide, ether, boiling alcohol, and essential oils, and not too costly—is anthracene.

The mode of preparing and using the filter is simple. Anthracene is slightly moistened with alcohol to make it miscible with water, diluted to the right consistency, and applied to the same apparatus, and in the same way, as the emulsion of asbestos which is employed in making asbestos felts. That is to say, enough of the emulsion in water to form a layer of the proper thickness is poured into a perforated crucible which is held tightly in a packing of rubber tubing stretched over a funnel fitted in the usual manner to a vacuum-flask or receiver. After washing with water the filter is ready for use. If the felt happens to be too coarse for the use of the moment, it may be made as close as need be by coating the felt first deposited with a finer emulsion, made by dissolving anthracene in hot alcohol and precipitating with water. When voluminous precipitates are to be filtered, the large perforated cone described in the former paper, to which I have referred, may be substituted with advantage for the crucible; or Cooke's improved form[1] of Carmichael's process of reverse filtration may prove most useful. In using the cone it is well to apply the anthracene in a thick layer.

To remove the anthracene filter from a precipitate it is only

[1] Proceedings of the American Academy **12**, 124.

necessary to act with the proper solvent. It is usually convenient to stand the crucible containing precipitate and felt in a small beaker, add enough of the solvent, and gently warm until the anthracene dissolves. On the addition of water, or the reagent to work upon the precipitate, the solution of anthracene floats, and nothing remains to obstruct or obscure the action. If the precipitate dissolves entirely, the solution of anthracene may be separated from the aqueous solution by simply pouring the fluid upon a filter previously moistened with water, when the solution in water runs through, and the anthracene and its solvent remain and may be washed indefinitely with water.

If, on the other hand, the case is one of the division of precipitates, the anthracene and its solvent may be made to pass the filter, after the water has run through, by adding a little alcohol to overcome the repulsion between the solution and the water which fills the pores of the filter, the precipitate which stays behind being washed first with a solvent of anthracene, and then, if necessary, with alcohol followed by water; or, if the vacuum filter be used (either paper or asbestos, according to the circumstances of the case), both liquids leave the precipitate and traverse the filter together.

In general I prefer benzol as the solvent for anthracene, but some advantage may be gained in special cases by a proper choice of solvents. Thus, in removing intermixed sulphur from precipitated sulphides, both the anthracene and the sulphur may be dissolved in carbon disulphide in a single operation.

The ready volatility of anthracene, at a temperature very near its melting point, 213° C., makes it easily separable in cases when to remove it by a solvent is not advisable. The treatment of a solution of anthracene, for example, with strong sulphuric or nitric acid is apt to produce carbonaceous or gummy residues. In such cases it is well either to heat precipitate and filter directly, or to first remove them from the crucible by means of a solvent for anthracene, then evaporate this and raise the heat gently until the anthracene has vanished. The purification of precipitated baric sulphate, by dissolving it in hot, strong sulphuric acid, and reprecipitating by dilution, is a case in point; and one, too, in which the reversed filter may be used with great advantage. It may be remarked, in passing, that if one does not happen to possess a platinum rose, and does happen to have at disposal a

perforated crucible, a very fair reversed filter may be improvised of the crucible, a piece of glass tubing, and a rubber stopper, the last being fitted to the crucible, and the tube passed through nearly to the perforated bottom.

At every point in the preparation and use of the anthracene filter I have found the manipulation peculiarly easy.

ELECTROLYSIS OF MOLYBDENUM SOLUTIONS.

By Edgar F. Smith and W. S. Hoskinson.

In a paper published by one of us (S.) in Vol. I, No. 5, of this Journal, attention was directed to the action of the electric current upon alkaline molybdic acid solutions. We there showed that although this method of precipitation was complete, yet the unusual time (100 hours) required rendered it practically useless. Since then we have found that by employing neutral solutions or such as contain a very slight excess of sulphuric acid, quite satisfactory results can be obtained.

The form in which the molybdenum separates on the crucible sides is as black $Mo_2O_3 3H_2O$, as already observed (Vol. I, No. 5). When the precipitation is complete the liquid is carefully siphoned off, the bright, compact coating washed with water, and the crucible with its deposit dried upon a water bath (about 90°) and weighed. It may be well to carefully ignite the black oxide in a covered crucible and thus convert it into trioxide, and weigh in the latter form.

In Volume 4 of the *Handwörterbuch der Chemie* it is stated that the electric current precipitates metallic molybdenum from solutions of ammonium molybdate. The determinations made by us under varying conditions do not confirm this statement. Our product in all instances was $Mo_2O_3 3H_2O$.

For our experiments we employed solutions containing different amounts of molybdenum. The precipitation was made in a platinum crucible of about 30 cc. capacity, although the dilution rarely exceeded 25 cc., so that space remained for exposure of fresh surface, and in this way afforded a ready means of knowing when

the precipitation was complete. The filtrate and washings from the deposit were always examined for molybdenum. The deposition of oxide occurs upon the zinc pole of the battery.

Experiments.

I. In a solution containing .0093 gram molybdenum as ammonium molybdate we obtained by electrolysis:

	$Mo_2O_3 . 3H_2O$.	Mo.
1.	.0146 gram.	.0095 gram.
2.	.0146	.0095
3.	.0138	.0090
4.	.0137	.0089
5.	.0138	.0090
6.	.0142	.0092
7.	.0143	.0093
8.	.0146	.0095
9.	.0146	.0095
10.	.0146	.0095

Molybdenum was not found in the filtrate. The time required for the above precipitations was two hours in each case. The current was obtained from four small-size Grove cells.

II. The solution contained .0156 gram of molybdenum. We obtained:

	$Mo_2O_3 . 3H_2O$.	Mo.
11.	.0236 gram.	.0154 gram.
12.	.0239	.0156
13.	.0245	.0160
14.	.0228	.0148

The time of precipitation was two hours. Used four Grove cells. No indications of molybdenum in any of the solutions after the deposition of oxide.

III. A solution containing .0167 gram molybdenum gave:

	$Mo_2O_3 . 3H_2O$.	Mo.
15.	.0256 gram.	.0167 gram.
16.	.0252	.0164
17.	.0258	.0168
18.	.0258	.0168
19.	.0257	.0166

Three hours were employed in precipitating the above quantities. Four Grove cells. Molybdenum not found on testing the filtrates.

IV. We found in a solution containing an unknown amount of molybdenum:

	$Mo_2O_3 . 3H_2O$.
20.	.0325 gram.
21.	.0329
22.	.0330
23.	.0315

The time was three hours. Employed the same battery power as in the other determinations; 23 is the only instance where molybdenum was detected.

The action of the current upon molybdenum solutions containing other metals is receiving study at present.

WITTENBERG COLLEGE, O., *April* 7, 1885.

ON THE DETECTION OF ADULTERATIONS IN OILS.

BY OSCAR C. S. CARTER.

The chemical examination of oils is a very important though much neglected study—important from the fact that the oils which command a high price in the market and are in general demand are frequently adulterated. The temptation to adulterate is great on account of the heavy increase in profit, and because the adulterant is often very difficult of detection. The purchaser is always at the mercy of the oil merchant, unless the oil be submitted to a chemical examination. "Our former Consul at Naples reported to the State Department that immense quantities of refined cotton seed oils are sent to Italy for the express purpose of sophisticating the native olive oil, for the reason that it can be brought to Naples and sold at less than half the cost of producing pure olive oil." The cotton seed oil mixed with pure olive oil is exported to other countries. The price of fine salad oil is from three to four dollars per gallon, while cotton seed oil is worth from seventy to ninety cents per gallon. The oils commonly used to adulterate olive oil are colza oil, sesame oil and peanut oil. In the North of France poppy oil is used frequently because of its cheapness and neutral taste, and in Provence honey is used. In all probability glucose

syrup has been tried. Linseed oil, the most important drying oil in the arts, so much used in varnishes and paints, is very often sophisticated. Even the seed from which the oil is made is mixed with other seeds. In India flaxseed is grown with mustard and rape. In Russia various proportions of hemp and linseed are sown together. Hemp seed yields an oil of an acrid odor, mild taste and yellow color, used in Russia for burning in lamps and making paints, varnishes and soap. The oils commonly mixed with linseed oil are niger, cotton seed, fish, rosin and coal oils. In this country lard is adulterated with palmnut and cocoanut oil; the latter is a white fat with the peculiar smell of the kernel. It was formerly made by grinding the kernel, boiling with water and subjecting the paste to a great pressure; a large quantity of milky juice is so obtained, which is slowly boiled and the oil separates and is skimmed off. Twenty ordinary sized nuts yield about two quarts of oil. The strong taste of these oils is an objection, and may prevent their general use as adulterants and for the manufacture of oleomargarine. Lard oil, which is obtained from lard, is very valuable as a lubricant for machinery, and is also used for greasing wool in spinning. It is frequently adulterated with fish oils and cotton seed oils. Lard oil is worth one dollar and twenty cents per gallon, while cotton seed oil is worth about one-half as much.

The chemical analysis and detection of the adulterated oil is sometimes simple, but generally it is a difficult and trying task, especially when three or more oils have been mixed. The determination of the percentage of oil used to adulterate is out of the question, and we must often be satisfied by simply proving that there has been a mixture without knowing the nature of it. But little work has been done on oils compared to the vast amount of research given to other subjects. Chemists have avoided the study and analysis of oils as difficult and uninteresting. We owe almost all we know to the labors of Chevreul, and later to the researches of Prof. Allen and others. When oils are examined, chemical tests are the more important, but the physical tests are also very useful. At the present time we have not a characteristic test for each oil, as we have for each metal, that will distinguish it when mixed with other oils or that will identify it when alone.

When we examine an oil supposed to be adulterated, much can be accomplished by procuring a sample of perfectly pure oil and subjecting them both to the same tests and observing their behavior.

A sample of lard oil supposed to be adulterated was received from a woollen manufacturer for examination. A specimen of perfectly pure lard oil was obtained and they were subjected to the same tests.

According to Professor Bechi, of Florence, the following test is reliable and delicate for detecting cotton seed oil in olive oil. The reagent is a one per cent. solution of nitrate of silver in absolute alcohol. Place 5 cc. of the suspected oil in a glass flask, add to it 25 cc. of absolute alcohol and 5 cc. of the test solution of nitrate of silver, made as stated above. The flask is heated in a water bath at 84° C. (direct heat must not be used). If there be any cotton seed oil present, the mixture will begin to darken, the most minute quantity serving to discolor, and the tint assumed will depend upon the amount of cotton seed oil present. The test depends upon the fact that cotton seed oil will reduce nitrate of silver, but olive oil will not. This reduction is also caused by rape seed oil, but according to Bechi, pure olive oil will remain without discoloration under this test. While experimenting with the test I thought it might be of service in detecting cotton seed oil in lard oil; accordingly the sample of chemically pure lard oil was treated with absolute alcohol and nitrate of silver as directed and then heated; there was not the slightest discoloration of the pure lard oil; even on standing for two weeks it did not darken, thus proving it had no action upon the nitrate of silver. The lard oil obtained from the woollen manufacturer was then tested in the same manner; when it had been heated for a few minutes it began to darken and finally became quite black, thus proving that the lard oil was not pure, but mixed with some other oil. I am not certain that the darkening is due to reduction; having made a series of experiments with salts of mercury, copper, and antimony and cotton seed oil to see if there would be any reduction I obtained no satisfactory results, and no reduction was noticed.

The elaidin test is sometimes very satisfactory, especially in detecting a mixture of a drying and non-drying oil and detecting adulteration of olive oil. This test depends upon the fact that olein and oleic acid in contact with peroxide of nitrogen yield a crystalline, solid, fatty body fusible at 32° C. to which Boudet has given the name elaidin. The nitrous vapors made by the action of nitric acid on copper are passed through the oil, or it may be shaken with a fresh solution of mercurous nitrate which has the

property of retaining nitrous acid. Non-drying vegetable oils and most animal fats contain oleic acid. The following oils contain a high percentage of olein: olive, almond, rape, arachis (earthnut), castor, and the oils from lard and tallow. These oils form with nitrogen peroxide solid elaidin of a white or yellow color, which in some cases is firm and resonant. The drying oils, such as linseed, hemp seed and poppy seed oils, do not form solid elaidin with nitrous vapors, but remain liquid for more than two days and become slightly colored. The elaidin test was applied to the adulterated lard oil and to the pure lard oil by adding an equal amount of nitric acid (sp. gr. 1.40) and some copper turnings. The elaidin produced by the pure oil was more firm and coherent than that of the adulterated oil and was of a lighter color; also the nitrous fumes rose more rapidly through the pure oil. One curious fact noticed about the adulterated lard oil was, it could not be completely saponified with caustic soda; even when the latter was added in excess, a clear layer of unsaponified oil remained after several trials. This test clearly indicated adulteration, as pure lard oil will completely saponify with caustic soda. Prof. Allen has proved that shark liver oil and African fish oil resist saponification. He tried to saponify the former oil with aqueous potash, with a solution of potash in absolute alcohol, and by heating it with solid potash, but it would not completely saponify; this he thinks is due to the fact that it contains a body allied to cholesterin, but fluid at ordinary temperatures.

Pure lard oil gives with nitric acid of sp. gr. 1.33 a yellow color, approaching orange.

The adulterated sample of lard oil with nitric acid of the same strength gave a distinct brown color on standing. That portion of the oil which resisted saponification with caustic soda was treated with nitric acid, and it soon became of a deep coffee-brown color, much darker than the above.

The determination of specific gravity is the most important of the physical tests. The viscosity of an oil is a highly important feature, but in order to be of any value in testing, much care must be observed; both oils must be brought to the same temperature, and kept so while flowing. Both the adulterated and the pure lard oil were subjected to this test; they were brought to a temperature of 80° F., and 5 cc. of each oil were passed through a capillary tube. The pure oil required 960 seconds to pass through,

while the adulterated oil required 1080 seconds. The experiment was repeated several times with different tubes, but the ratio of the times of flowing was constant. Both oils were subjected to a temperature of 32° F. When the pure oil was frozen it was more coherent and firm and much lighter in color; the adulterated sample was quite yellow. When the adulterated oil slowly became liquid a layer of yellow oil formed first, which was quite different in appearance from the other portion and was evidently the adulterant.

While we cannot depend on any single test, the evidence afforded by several is often conclusive and satisfactory, and in this case it was acknowledged afterwards that cotton seed oil was one of the adulterants.

CENTRAL HIGH SCHOOL, PHILA.

ON THE UNIT USED IN CALCULATING THE ATOMIC WEIGHTS.[1]

BY LOTHAR MEYER AND KARL SEUBERT.

The controversy arising immediately after the proposal of Dalton's atomic theory, as to the unit upon which the numerical values of the atomic weights should be based, has for a half-century divided chemists into two schools. While Dalton and, later, Leopold Gmelin, from theoretical and philosophical considerations, chose the smallest atomic weight, that of hydrogen, as the measure of all the rest, Wollaston and Berzelius chose that of oxygen, partly because they did not place so high a value on theoretical views, partly and especially on the purely practical ground that many elements can be compared directly with oxygen, whereas they can be only indirectly compared with hydrogen. When the Dalton unit, the hydrogen atom, gradually obtained the upper hand, the old controversy appeared to have been laid aside, and consequently it was to be hoped that the recent more exact investigations of the laws which govern the numerical values of the atomic weights would be directed from the same point of view.

[1] Translated by W. S. Bayley from an article in the Berichte der deutschen chemischen Gesellschaft **18**, 1089.

This hope, however, has unfortunately not been fulfilled, as the old Wollaston-Berzelius unit has lately again come into use in a different and, as we believe, more dangerous form.

As is well known, J. S. Stas[1] has, from his own observations as well as those of others, deduced as the most highly probable result, that the atomic weight of oxygen is not quite sixteen times as great as that of hydrogen, but on the contrary is about $\frac{1}{100}$ of its value less than 16H. This follows:

(1) From the numerous gas analyses (reduced to weight) conducted since the discovery of Gay Lussac and von Humboldt, or, what amounts to the same thing, from Avogadro's law and the experimentally determined densities of both gases (No. 1 a,[2] and Julius Thomsen, Berichte der deutschen chemischen Gesellschaft, 3, 927);

(2) From the synthesis of water by means of copper oxide (*loc. cit.* No. 1 c, d);

(3) From the relations of sal ammoniac to silver nitrate and of both to silver (*ib.* No. 47 and 83), where, as confirmatory of the atomic weight of nitrogen (N = 0.87791O) used in the calculations, the relations of the chlorides and metals to the nitrates could also be determined (No. 131, 132, 133, 135); and further, though with somewhat less certainty,

(4) From the relation of the crystallised and dehydrated strontium chlorides to each other and to silver (No. 65 c and 140);

(5) From the relation of these substances to each other and to the sulphate (No. 197);

(6) From the corresponding numbers for crystallised and dehydrated barium chloride and silver (No. 66 e and 141);

(7) From the relation of both forms of barium chloride to the sulphate (No. 188 d);

(8) From the relation of aluminium to hydrogen and to water (No. 8 c, d and 144).

The determinations deduced from methods 1 and 2, undoubtedly the most exact, give as a mean the ratio

$$H : O = 0.06265 : 1 = 1 : 15.96$$

which Stas considered as coming nearest to the truth. The simple ratio of 1 to 16 demanded by Prout's hypothesis in one

[1] Nouvelles recherches sur les lois des proportions chimiques. Bruxelles, 1865, p. 24, etc.

[2] Die Atomgewichte der Elemente aus den Originalzahlen neu berechnet, von L. Meyer und K. Seubert. Leipzig, 1883.

sense lies entirely outside of the observed values, in another sense very near to their extreme limits. To an unprejudiced judge not biassed in favor of that hypothesis, not yet established by the best observations, there appears no ground for accepting this numerical relation rather than that obtained as the mean value.

Further, if the simpler ratio be accepted, the experiments embraced under the heads from 3 to 8 yield results almost all of which agree less well than if the more complex ratios were accepted, and the differences between the calculated values and those obtained under 3 are greater than could be accounted for on the supposition that they are due to errors of observation.

But since this relation between the atomic weights of hydrogen and oxygen had not yet been as accurately determined as that of other elements to one another, Stas, in order to show the utter indefensibility of Prout's hypothesis, calculated all the atomic weights determined by him upon the assumption, *incorrect according to his opinion*, that the atomic weight of oxygen is just sixteen times as great as that of hydrogen. He pointed out that even with this assumption Prout's hypothesis would not hold good for the rest of the atomic weights under investigation. This supposition, made by Stas merely for the sake of argument, appears to have been much misunderstood; as if the value O = 15.96 and O = 16.00 were exactly the same, which of course is not at all the case. It is rather in a high degree probable, if not certain, that the number 16 is incorrect to 3 or 5 units in the second decimal place, whereas the other value 15.99 is out only 1 or, at the most, not more than 2 units.

Since we were at that time accustomed to reckon with O = 16, and Stas naturally discussed only those atomic weights which had been newly determined by him, the choice was offered whether to calculate all atomic weights with the corrected values of oxygen, silver, chlorine, etc., as a basis, or provisionally to manage further with the old numbers, and merely introduce the corrected atomic weights of Stas into a system resting upon a somewhat more defective basis. This last, incorrect indeed, but more convenient way, was chosen by many chemists. This could the more easily be done since most of the atomic weights in use at that time were justly looked upon as not being very accurate, and a difference of $\frac{1}{400}$ of a value was of very little practical consideration.

The hope that at least the old controversy over the choice of

the unit would disappear upon a recalculation of the atomic weights of all the elements, has unfortunately not been fulfilled. There is a universal desire to do away with the unit preferred by Thomsen, Wollaston and Berzelius,

$$O = 1, = 10 \text{ or } = 100,$$

and to refer all atomic weights to hydrogen. But as to the way in which this should be done, opinions differ. With a few exceptions (as in the case of Al, No. 8 c, d), the relation to hydrogen is deduced only through the intervention of oxygen, consequently the numerical values of all atomic weights depend upon that of oxygen. In consideration of this we have, in our recalculation of the atomic weights referred to above, made use of the Wollaston-Berzelius unit ($O = 1$), as well as the usual one ($H = 1$), so that in case of a new, more trustworthy determination of the relation O : H, the numbers referred to hydrogen as 1 could easily be corrected. A few years earlier G. F. Becker[1] referred all the atomic weights to $O = 16$. F. W. Clarke[2] has, like us, taken $H = 1$, but has also, out of fondness for Prout's hypothesis, given a table in which $O = 16$ and consequently $H = 1.0023$. J. Sebelin[3] makes use of the same units as we do ($H = 1$ and $O = 100$), and only occasionally adds a few numbers calculated on the supposition that $O = 16$. W. Ostwald[4] does not agree with Stas that the value $O = 16$ is too large, but thinks that, from the last five observations of Erdmann and Marchand,[5] the first three of which he casts aside, it must follow that for $H = 1$, O must be exactly 16.00, though the sum of all the experiments of these authors gives $O = 15.96$. J. D. van der Plaats[6] inclines to the view that O may be equal to 16, though he considers the question as still open. W. Dittmar[7] has recalculated the atomic weights, calculated by us on the basis $H = 1$, on the basis $O = 16$ and $H = 1.0024$.

In consequence of these different views, all the other atomic weights fluctuate to the extent of about $\frac{1}{4}$ per cent. of their value,

[1] Atomic Weight Determinations; a digest of the investigations published since 1814. Washington, Smithsonian Institution, 1880.

[2] A Recalculation of the Atomic Weights. Washington, Smithsonian Inst. 1882.

[3] Beiträge zur Geschichte der Atomgewichte. Preisschrift, Braunschweig, 1884.

[4] Lehrbuch der allgemeinen Chemie. Leipzig, 1884.

[5] Meyer and Seubert, No. 1 d; Clarke, p. 5.

[6] Comptes Rendus, Jan. 5, 1885, 100.

[7] Tables to facilitate chemical calculations. 2d Ed. Glasgow, 1885.

amounting in the case of the largest to one-half of the unit. That such a condition of things is undesirable, all scientific men are agreed, and also, that the very smallness of the difference aids in the confusion and perplexity, since every author will not state, in every article, the standard according to which he calculates.

How the evil is to be remedied is difficult to say. First of all it is to be remembered that both values for the atomic weight of oxygen lie within the limits of errors of observation, and that, in case authenticated constant errors tend to lower the result, it may even be admissible to take the maximum value O = 16.03 instead of the mean value O = 15.96. It is more questionable, however, to round off this maximum value just at the number 16, for which there are no grounds except the unproven Prout's hypothesis. The secret or confessed fondness for this hypothesis is probably the true cause of the choice of this number. We willingly acknowledge that there may be concealed in this hypothesis of Prout's a valuable idea; but this does not change the fact that, *as now stated, the hypothesis is untenable.* Wherever up to this time the proof has been looked into with sufficient exactness, it has shown that the atomic weights are not exact multiples of whole numbers, and this result is independent of the relation of oxygen to hydrogen. Accept this or not as we will, we always obtain for the atomic weights, when most accurately determined, irrational numbers.

What seems to be most noteworthy in Prout's hypothesis is brought into view, and in an unprejudiced manner, when we take the relation of H : O as given by the most accurate observations. For instance, it is a striking fact that the atomic weights of more than one-fourth of all the elements are very nearly multiples of the half atomic, or equivalent weight of oxygen, as the following table will show.

Multiples of $\frac{1}{2}O = 7.98$.

Factor.	Product.	Atomic Weights.	Difference.
1	7.98	...	...
2	15.96	O = 15.96	0
3	23.94	Mg = 23.94	0
4	31.92	S = 31.98	+ 0.06
5	39.90	Ca = 39.91	+ 0.01
6	47.88	Ti = 48.01	+ 0.13
7	55.86	Fe = 55.88	+ 0.02
8	63.84	(Cu = 63.18)	(— 0.66)
9	71.82	Ekasilicon.	...
10	79.80	Br = 79.76	— 0.04
11	87.78	(Sr = 87.3)	(— 0.48)
12	95.76	Mo = 95.9	+ 0.14
13	103.74	Ru = 103.5	— 0.24
14	111.72	Cd = 111.7	0
15	119.70	Sb = 119.6	— 0.10
16	127.68	...	...
17	135.66	...	...
18	143.64	Di = ?	...
19	151.62	Break in VI.	...
20	159.60	...	...
21	167.58	Eb = ?	...
22	175.56	Break in IV.	...
23	183.54	W = 183.6	+ 0.06
24	191.52	Os = ?	...
25	199.50	Hg = 199.8	+ 0.3
26	207.48	Bi = 207.3	— 0.18
27	215.46	...	...
28	223.44	...	...
29	231.42	Th = 231.96	+ 0.54
30	239.40	U = 239.8	+ 0.4

Such regularities are worthy of note; but to attempt to correct the atomic weights by them would be just as incorrect as to round them off into whole numbers.

He who does not adhere to Prout's hypothesis, and is besides not of the opinion that the observations yield as the most probable value of the relation O : H = 16 : 1, has, according to our view, not the least ground for giving the value O = 16 the preference over O = 15.96. Then, if we take the atomic weight of oxygen, not as = 1 or = 10 or = 100, but as = 16, the only meaning that can be attached to it is, that it appears more proper to take the hydrogen atom as the unit. This view is universally held; but since its relation to oxygen is uncertain to a few thousandths of its value, it is thought that the round number 16 may be used instead of the 15.96 found, though it is necessary in this case to place H = 1.0025, *i. e.* to take as the unit $\frac{399}{400}$ of the

atomic weight of hydrogen. Such a wonderful unit can only be endured in the quiet hope of the future fulfilment of the hypothesis of Prout. In the end hardly any one will seriously wish science to be burdened with it.

It is admitted that with the atomic weight of oxygen uncertain, all others remain so likewise in the fourth and following places of their numerical values, while their relative values, their relations to one another, in many cases are correctly determined to the fourth, and in some cases even to the fifth place. These facts can be changed by no hypothetical considerations. If to-morrow the relation O : H should be determined more accurately to the one or two thousandth part of its value, and this number should differ from the one accepted to-day, all the other atomic weights would have to be recalculated.

What advantage is offered in calculating with H = 1.0025 and O = 16 we cannot possibly see. The fact that the numerical values for oxygen, carbon and a few other elements are thereby reduced to two figures, can hardly appear so desirable that one should, for this reason, consent to the choice of such a nonsensical unit.

It has been stated that the error which would be introduced by making H = 1 is much smaller than the unavoidable errors of observation.

But so far as this is concerned, it may on the other hand be asked: Why introduce even so small an error when it can be avoided? Our observations are, without this, already sufficiently subject to sources of errors of all kinds. It does not change the case at all if the omission of these small fractions does *not* influence the decimal places which are generally considered in analysis. If for most *inorganic* compounds no difference of importance is effected, in the case of the analysis of *organic* compounds it is otherwise.

In this field no one would be expected to reckon with H = 1.0025. After H has once been decided upon as = 1, it makes quite a difference in the result whether O is taken as 15.96 and C as 11.97, or O as 16 and C as 12. In some cases this difference is greater than the difference in the composition of closely related compounds.

The table given below shows the percentages of hydrogen and carbon in the paraffins containing 30 and 31 carbon atoms and

their derived alcohols and acids (myricyl alcohol and melissic acid[1]), and also the amount of water and carbon dioxide produced in their combustion. Under *a* are the results calculated with O = 15.96, C = 11.97, under *b* with O = 16 and C = 12.

	H_2O		H		CO_2		C	
	a	*b*	*a*	*b*	*a*	*b*	*a*	*b*
$C_{30}H_{62}$	132.22	132.23	14.723	14.692	312.68	312.80	85.277	85.308
$C_{31}H_{64}$	132.10	132.11	14.710	14.679	312.73	312.84	85.290	85.321
$C_{30}H_{60}O$	127.39	127.40	14.186	14.155	301.26	301.37	82.163	82.192
$C_{31}H_{62}O$	127.42	127.43	14.190	14.159	301.66	301.77	82.272	82.301
$C_{30}H_{60}O_2$	119.46	119.47	13.303	13.274	291.94	292.04	79.620	79.646
$C_{31}H_{62}O_2$	119.74	119.74	13.334	13.305	292.61	292.70	79.802	79.828

Thus we see that the amount of water remains almost the same in each calculation because the variations compensate each other; the hydrogen on the other hand varies a few hundredths, as does also the carbon, while the variations in the carbon dioxide reach the tenths of a per cent., *a difference which is often greater than that obtained from two adjacent hydrocarbons in a homologous series.* This last is more clearly seen if we calculate by both methods the percentages of carbon and dioxide contained in a series of hydrocarbons, and place them together as is done in the following table.

		$C_{24}H_{50}$	$C_{25}H_{52}$	$C_{26}H_{54}$	$C_{27}H_{56}$	$C_{28}H_{58}$	$C_{29}H_{60}$	$C_{30}H_{62}$
C	*a*	85.176	85.196	85.214	85.232	85.248	85.263	85.277
	b	85.207	85.227	85.246	85.263	85.279	85.294	85.308
CO_2	*a*	312.310	312.384	312.452	312.516	312.575	312.630	312.681
	b	314.426	312.500	312.568	312.632	312.690	312.745	312.796

This shows that the different calculations *a* and *b* may lead to different interpretations of the analyses. If, for instance, the combustion of a hydrocarbon yields 312.51 mg. of carbon dioxide for every 100 mg. of substance, the advocate of Prout's hypothesis will find that the formula $C_{28}H_{58}$ best expresses the result of the analysis, while according to Stas and his followers it indicates the formula $C_{27}H_{56}$. Of course, no one would determine the formula of such a body by means of analysis alone; still, one is accustomed in the choice of formulas to lay a certain weight on the mean result of a series of closely agreeing analyses, and this would here lead to a false conclusion if an error of a few thousandths

[1] Cf. F. Schwalb, Ueber die nicht sauren Bestandtheile des Bienenwachses. Inaug. Diss. Tübingen, 1884.

in the atomic weight of hydrogen were not thought worthy of account.

Those who think with us that the determinations thus far submitted render more probable the relation

$$O : H = 15.96 : 1 = 1 : 0.06265,$$

than that demanded by Prout's hypothesis,

$$O : H = 16 : 1 = 1 : 0.06250,$$

are guilty of a dangerous inconsistency when they operate with such atomic weights as

$$O = 16,\ C = 12,\ Cl = 35.46 \text{ or even } 35.5, \text{ etc.}$$

These may, of course, be used in the laboratory for the calculation of approximate results, as in the case of preparing substances; but when it comes to calculating accurate analyses they should not be used.

We may ask of the admirers of Prout's hypothesis whether the universal acceptance of a uniform basis for all atomic weight determinations is not of much more value than a supposition which, in a few cases, may possibly not be entirely erroneous?

We are all convinced that the relation under consideration (and thereby every other atomic weight referred to $H = 1$) is not accurate to the thousandth part of its value. Let us accept it without artificial interpretations, just as it is yielded as the mean value of agreeing results obtained in many different ways, and wait till the future for its further proof and confirmation by experimental methods. As soon as this is accomplished we will be ready, among the first, to accept any changes in the values of the atomic weights as now calculated that may then be deemed necessary.

THE ATOMIC WEIGHT OF SILVER AND PROUT'S HYPOTHESIS.[1]

By Lothar Meyer and K. Seubert.

The calculation of the atomic weights of many of the elements depends, as is well known, upon that of silver, so that the sharpest possible determination of this is desirable in order to obtain

[1] See Berichte der deutschen chemischen Gesellschaft **18**, 1098. Translated by W. S. Bayley.

accurate results, without which a discussion of Prout's hypothesis, *as far as this is concerned with facts*, is unprofitable.

For this reason J. S. Stas, in his masterly investigations, used the utmost care in fixing the stoichiometrical relations between silver and oxygen, and confirmed these by indirect methods with wonderful accuracy. The hypothesis of Prout, that all atomic weights are rational multiples of that of hydrogen, is not borne out by Stas' work; even when the relation of oxygen to hydrogen = 15.96 : 1 is rejected as doubtful and 16 : 1 is taken in its stead, silver and a number of other elements, among them those whose ratio to hydrogen is most accurately known, differ in their atomic weights far more from whole numbers than experimental errors can account for. The accuracy and reliability of Stas' results seemed so far beyond all doubt that one of the most celebrated advocates of Prout's hypothesis could explain the contradiction of the theory by the experiments only by questioning the stability of the foundation of the atomic theory, *the constancy of chemical proportions*, and consequently the possibility of preparing chemically pure substances.[1]

In 1878 Dumas,[2] also a supporter of Prout's teaching, published the results of a few experiments, in which he succeeded in separating oxygen from pure silver which had been fused with a mixture of borax and saltpeter. A kilogram of the silver was heated to redness in a flask connected with a Sprengel's pump, and the evolved oxygen collected and measured.

For each kilogram of silver there were obtained in four different experiments 82, 226, 140 and 249 milligrams of oxygen.

As Stas subjected the silver used in his investigations to the same treatment, this too, as Dumas claimed, must have contained oxygen. In spite of all the care and skill of the experimenter, his results with metallic silver were affected by a constant error which increased the atomic weight of the silver and lowered those of the halogens; the relation of silver to chlorine instead of being 108 : 35.47 as was then generally believed, became 108 : 35.5, in accordance with Prout's hypothesis.[3]

[1] Marignac, Archives des sciences physiques et naturelles (nouv. pér.) **9**, 1860, p. 105 and ff. "Il ne m'est pas absolument démonstré, que bien des corps composés ne renferment pas constamment et normalement un excès, très faible sans doute, mais sensible dans des expériences très-délicates, de l'un de leurs éléments." See also Ann. Chem., Suppl. IV, p. 202.

[2] Compt. rend. **86**, 65-71. Ann. chim. phys. [5], **14**, 289.

[3] A conclusion of Dumas' which can be contested on more grounds than one. See below.

It cannot be denied that this objection is worthy of attention, and we are justified consequently in briefly considering its effect on the result by briefly discussing a few experiments.

If Stas really worked with silver containing oxygen his error will consist in this, that instead of using 1000 parts of silver he used only 999.751 parts.[1] In transforming silver into silver chloride, Stas obtained by four different methods,[2]

from 969.3548 grams Ag 1287.7420 grams AgCl,
in which Ag : AgCl = 1 : 1.32845.

This relation is changed by Dumas' correction into

969.1134 grams Ag = 1287.7420 grams AgCl,
or Ag : AgCl = 1 : 1.32872.

In the same way the correction may be applied to the cases in which silver was changed into silver bromide or iodide by synthesis. In all these cases the error might possibly have reached the maximum as observed by Dumas.

Fortunately, however, a number of experiments were made from which the amount of oxygen contained in the silver can be determined. These consist of *complete syntheses of silver bromide and silver iodide*, when the amounts of both constituents used as well as the resulting compound were weighed.

In both cases the weight of the product was found to be somewhat too low, a result which can be referred to the oxygen in the silver.[3]

The complete synthesis of the silver bromide yielded these figures:[4]

Ag : Br : AgBr = 210.5711 : 156.0098 : 366.5639 grams [4]

Ag + Br =	366.5809
AgBr =	366.5639
Difference,	.0170

Calculated for the amount of silver used, this difference corresponds to 0.08073 pts. of oxygen in 1000 pts. of silver, provided the

[1] In the most unfavorable case, when the silver contains the largest amount of oxygen observed by Dumas, viz. 0.249 pts. per 1000.

[2] Lothar Meyer and Karl Seubert, Die Atomgewichte der Elemente. Leipzig, 1883, p. 55 and 56, No. 41 g.

[3] As the difference in the case of the synthesis of silver bromide was smaller the more carefully the bromine was dried, this must in part be due to moisture in the bromine. Besides there was a small loss occasioned by washing.

[4] Die Atomgewichte der Elemente, etc., p. 57, No. 42, b. β.

total loss were due to escape of oxygen. The corrected weight of the silver then becomes 210.5541 grams.

$$\text{Then Ag} : \text{AgBr} = 210.5541 : 366.5639$$
$$= 1 : 1.74095$$
$$\text{instead of } 1 : 1.74081$$

Similarly, in the complete synthesis of silver iodide the weight of the product is less than the sum of the weights of iodine and silver.

Stas found[1]

$$\text{Ag} : \text{I} : \text{AgI} = 324.2571 : 381.1262 : 705.3718 \text{ grams} \qquad [5]$$
$$\text{Ag} + \text{I} = 705.3833$$
$$\text{AgI} = 705.3718$$
$$\text{Difference,} \quad .0115$$

This difference corresponds to .03547 parts of oxygen in 1000 of silver, so that the weight of pure silver used was 324.2456 grams. Consequently,

$$\text{Ag} : \text{AgI} = 324.2456 : 705.3718$$
$$= 1 : 2.17542$$
$$\text{instead of} = 1 : 2.17535$$

The comparison of these values with those obtained from the analyses of the chlorates, bromates and iodates gives the relation of silver to oxygen.

Stas found

$$\text{AgClO}_3 : \text{AgCl} = 398.3177 : 298.4250 \text{ grams}^2 \qquad [2]$$
$$\text{AgBrO}_3 : \text{AgBr} = 188.5332 : 150.1671 \text{ grams}^3 \qquad [2]$$
$$\text{AgIO}_3 : \text{AgI} = 331.6101 : 275.3235 \text{ grams}^4 \qquad [3]$$
$$\text{Or,} \quad \text{AgCl} : \text{O} = 8.9614 : 1$$
$$\text{AgBr} : \text{O} = 11.7420 : 1$$
$$\text{AgI} : \text{O} = 14.6742 : 1$$

Evidently these figures cannot be influenced by Dumas' correction, as there was no metallic silver weighed. From these figures the relation of the silver to the oxygen can easily be calculated by means of the formula[5]

$$\frac{\text{Ag}}{\text{AgR}} \cdot \frac{\text{AgR}}{\text{O}} = \frac{\text{Ag}}{\text{O}},$$

[1] Die Atomgewichte der Elemente, etc., p. 59, No. 43 b. γ.
[2] *Ibid.* p. 47, No. 35 b.
[3] *Ibid.* p. 47, No. 36.
[4] *Ibid.* p. 48, No. 37 b.
[5] *Ibid.* pp. 50-52.

in which R is one of the halogens Cl, Br or I. According to this,

$$Ag : O = \frac{8.9614}{1.32872} = 6.7439 : 1$$

$$Ag : O = \frac{11.742}{1.74095} = 6.7446 : 1$$

$$Ag : O = \frac{14.6742}{2.17542} = 6.7455 : 1$$

Of these three numbers, neither of which agrees with the 6.7500 demanded by Prout's hypothesis, the third is entitled to most consideration; for, in the first an arbitrary correction is made, in the second a part of the error credited to oxygen must surely be due to some other impurity, the third is calculated from experiments made with the purest materials. This number 6.7455, obtained from the complete synthesis of silver iodide and the analysis of the iodate, is also the mean of several other determinations made by Stas which vary between 6.7451 and 6.7458; besides, it is almost identical with 6.7456 yielded by silver iodide and iodate without the application of Dumas' correction, as well as the 6.7456 obtained by reducing silver sulphide and sulphate.

The conclusion is consequently justified, since several of Stas' determinations agree satisfactorily with one another and with the number which is certainly free from the error pointed out by Dumas, that the influence of this is confined within the limits of error and consequently may be neglected.

If it appears strange that the silver used by Stas for determining the atomic weight exhibited only in small degree an impurity, whose amount was determined by the experiments of Dumas as being quite considerable, it must be remembered that only the oxygen present in a condensed form would influence the weight; the gaseous oxygen under the normal pressure producing an effect scarcely more noticeable than the air in which the silver was weighed. Besides, Stas always heated his silver to dark redness immediately before weighing, so that the greater part of the "occluded" oxygen either escaped or was changed into the gaseous form.

These considerations, based on the results of experiments, show, as we again emphasize, *that the determinations of the atomic weight of silver by Stas are not appreciably influenced by the oxygen which the silver retains within itself.*[1]

[1] W. Ostwald reached the same conclusion through the theory of probabilities. See his Lehrbuch der allgemeinen Chemie, 1884, **1**, 35.

The atomic weight of silver then is, if H = 1 and O = 15.96,

$$Ag = 107.66$$

if O = 16, Ag = 107.93;

while the figures calculated from the results of the experiments with metallic silver and silver chloride are, after applying the correction of Dumas,

$$Ag = 107.63, \text{ if } O = 15.96, \text{ and}$$
$$Ag = 107.90, \text{ if } O = 16.00.$$

Thus we see that the atomic weight of silver is removed still farther from the whole number required by Prout's hypothesis, by the application of Dumas' correction; chlorine also still remains inconsistent with it, while a few other elements, like potassium, sodium, etc., approach or depart from it according as we take O = 16 or 15.96. Dumas has assumed, in order to explain such exceptions to Prout's hypothesis as chlorine particularly offers, that hydrogen itself is composed of ultimate atoms (uratomen), of which he at first thinks there are two in one atom of hydrogen, but when this is also found not to be in accordance with the experimental results, increases the number to four.

But even this "elastic modification," as Clarke calls it, of the old theory can only be preserved, in the face of Stas' work, by decreasing the size of the unit, that is the weight of the ultimate atom, in proportion as the accuracy of our experimental work increases.

More recently,[1] the universal ether, with an atomic weight of 0.0001 (H = 1), has been assumed as the primitive substance of which all other elements were formed. The atomic weights of all other elements must of course be whole multiples of this, since none of them have been accurately determined to the fourth decimal place, while many are certain only to the first or second place, and some only to units of hydrogen.

Nor need it excite wonder if, as has been proposed by another writer,[2] every atomic weight y can be approximately calculated by the expression:

$$y = p\,15 - 15\,(0.9375)^x \text{ or,}$$
$$y = 15\left(p - \left(\frac{15}{16}\right)^x\right),$$

[1] M. Zängerle, Über die Natur der Elemente, etc. Programm des Kgl. Realgym. München, 1882.

[2] Edm. J. Mills, On the Numerics of the Elements, Philos. Mag., Nov. 1884, p. 393.

in which p may vary between 1 and 16, but x varies from 1–50, or even ∞ ; for the fraction $\frac{15}{16}$ so nearly approaches unity that any number can be accurately expressed by the formula.

Speculations of this kind are far removed from any possibility of experimental proof, and can therefore never be expected to receive from it any support. Nor can we ever hope to receive any essential extension of our knowledge in respect to primitive matter (urmaterie) through a more accurate establishment of the atomic weights; the next important progress will rather be brought about by the decomposition of the elements into a similar substance, differing from them however, which may be the primitive matter itself, or a condensation product of it. The solution of this question, that is, the decomposition of all the elements into one and the same original substance, we can hardly ever expect to accomplish.

From the atomic weight of silver, determined, as above shown, with the greatest accuracy, and from those of the other important elements[1] calculated by its means, it follows as a consequence that *the atomic weight of silver, as well as the atomic weights of numerous other elements, all contradict Prout's hypothesis in its characteristic original conception; it must therefore be looked upon as having been disproved by experiment.* In its new forms it has likewise been disproved, so far as this is possible in the present state of our knowledge. Beyond this it amounts merely to philosophical speculation concerning an idea whose probable correctness will be denied by no one,[2]—the unity of matter.

EYSTER'S SCHEME FOR QUALITATIVE ANALYSIS.

By Robt. B. Warder.

In the last number of this Journal (pp. 21–26) appears a method for the qualitative determination of the bases without direct use of hydrogen sulphide, which will prove very convenient in many

[1] Cf. Atomic weight tables of Meyer and Seubert. Breitkopf u. Härtel, Leipzig, 1884.
[2] Cf. Lothar Meyer, Moderne Theorien, V. Auf. p. 134.

cases. Having used this method in part with my own classes during the past year, a few notes may be of service to those who have not yet tried it.

The use of sulphuric acid to precipitate Ba, Sr, Ca and Pb (as copied from Zettnow's scheme) appears to be a needless complication and may be simply omitted, other provision being made for the detection of these metals.

The principle underlying Eyster's most important modification will be seen at a glance from the following table; from which also an outline of the scheme may be deduced.

Basis of Usual Scheme.		Basis of Eyster's Scheme.		
Sulphides precipitated by H_2S in presence of HCl.	Sol. in Am_2S	As, Sb, Sn		Sulphides sol. in Am_2S.
	Insol. in Am_2S	Hg, Pb, Bi, Cd, Cu	Insol. in cold dilute HCl	Sulphides (or hydrates) precipitated by AmOH and Am_2S.
Not precipitated by H_2S in presence of HCl.		Ni, Co, Zn, Mn, Fe, Al, Cr	Sol. in cold dilute HCl	

Cobalt and nickel hold an exceptional position, their sulphides being practically insoluble in cold dilute chlorhydric acid, and yet not precipitated in presence of that reagent by hydrogen sulphide. Under the new scheme they are dissolved by nitric acid, and held in solution by excess of ammonia with the cadmium and copper. Eyster precipitates the four sulphides (after testing for Cu with ferrocyanide), dissolves the cadmium with sulphuric acid, and tests for nickel with the bead in presence of copper. My own experiments show that cadmium may also be separated from nickel and cobalt by adding ammonium sulphide in presence of potassium cyanide, and the following provisional scheme is offered:

Add KCy and Am_2S, yellow precipitate, *cadmium.*
Add $C_2H_4O_2$ to filtrate, black precipitate, *copper.*
Add HCl to filtrate, black precipitate, *nickel.*
Look for Co in solution.

This use of acetic and chlorhydric acids was proposed by Mr. J. Swearingen, and has been partially tested in this laboratory by himself and by Mr. E. G. Eberhardt. Acetic acid precipitates copper at once; a part of the cobalt also separates on standing one or two days.

In a mixture of cobalt and nickel sulphides, the former (as is well known) can usually be detected at once with the borax bead. The latter may be partly dissolved in yellow ammonium sulphide and reprecipitated by chlorhydric acid. I have rarely failed to obtain a sufficient quantity of nickel by this means to give distinct color to the bead.

Details will be found in Eyster's careful paper, which has induced me to present these notes at once, instead of waiting to make a more thorough examination of the special features proposed.

PURDIN UNIVERSITY, LAFAYETTE, IND., *May* 9, 1885.

ESTIMATION OF ARSENIC IN ORES, MATTES AND METALLIC COPPER.

BY G. W. LEHMANN AND W. MAGER.

In the course of professional work at our laboratory it has become necessary to determine small quantities of arsenic, and after testing the methods proposed for this purpose, we have found that proposed by R. Pearce[1] to be the most reliable and convenient. This consists in mixing the finely powdered substance with about six times its weight of equal parts of sodium carbonate and potassium nitrate, fusing and extracting with hot water, and filtering. The filtrate is then acidified with nitric acid, and boiled to expel carbonic and nitrous acids. To the cool solution silver nitrate is added, and then ammonia to neutral reaction. The silver arsenate is filtered, washed out with cold water until no silver is found in the washings, and the silver determined by Volhard's method. 108 parts of silver correspond to 25 parts of arsenic. Numerous experiments

[1] See Engineering and Mining Journal, May 5th, 1883, p. 256.

with ores and mattes (free of arsenic) mixed with known quantities of chemically pure arsenious oxide, and containing lead, antimony and aluminium salts (purposely added), convinced us of the accuracy of the method. Now the question arose how this method could be best applied to metallic copper containing about one-tenth per cent. of arsenic.

We found it most convenient to precipitate the arsenic in combination with oxide of iron. Considering that metallic copper very rarely is free from arsenic, and that borings taken from different parts of the same ingot contain different quantities of arsenic, we dissolved in each case 100 grams of copper in nitric acid, diluted to 500 cc. with water, and took 100 cc. (20 grams) for each determination.

In the first 100 cc. we determined the arsenic contained in the copper; to the second and third 100 cc. we added known quantities of arsenic which had been prepared by fusing chemically pure arsenious oxide with sodium carbonate and potassium nitrate and dissolved in nitric acid, and deducted the first result from the last. We proceeded in the following way: A piece of iron sulphate, about the size of a pea, was dissolved in nitric acid, added to the copper solution, and then ammonia in excess; the solution was well stirred and the precipitate of oxide of iron filtered hot, washed out with hot water, dried, removed carefully from the filter, mixed with the fusing mixture, etc. In another series of experiments we added lead and antimony, and found that their presence did not interfere with the results. (A solution containing both metals in considerable quantity gave 0.131 per cent. and .144 per cent. arsenic, when 0.134 per cent. arsenic was present.)

The following results show the accuracy of the method:

As present.	As found.	
0.0701 per cent.	0.0615 per cent.	0.0596 per cent.
2.87 "	2.82 "	2.94 "

0.0118 gram As_2O_3 (used in these experiments) gave .00907 gram As. Calculated .00894 gram As.

As present.	As found.	
0.1 per cent.	0.1004 per cent.	$AsMg(NH_4)AsO_4 = .092$ per cent.
	0.0953 "	

MINOR INVESTIGATIONS.

By L. M. Norton.

I. *Oxidation of Benzol.*

The action of a powerful oxidising agent upon benzol has been occasionally investigated, but the unexpected results obtained in certain cases have hardly attracted the attention they deserve. The formation of benzoic acid by the oxidation of benzol is certainly worthy of notice. Under my direction Mr. J. G. Holder has repeated some previous experiments in this direction, and we have also attempted the oxidation of benzol by some methods not heretofore employed. I give a summary of our experiments. The benzol used in all the experiments boiled between 80.2° and 80.3°, and left no residue at the latter temperature. Our analysis gave figures which corresponded to 92.20 per cent. of carbon and 7.70 per cent. of hydrogen, while the theory requires 92.30 per cent. of carbon and 7.70 per cent. of hydrogen. Its perfect freedom from toluol is certain, as long continued boiling with dilute nitric acid and also with a solution of chromic acid in acetic acid failed to furnish the least trace of benzoic acid. Carius[1] first investigated the action of binoxide of manganese and sulphuric acid upon benzol and obtained carbonic anhydride, formic acid, benzoic acid and a phthalic acid. We investigated this method of oxidation under somewhat different conditions with a somewhat different result. Three large flasks were taken and 100 grams of benzol placed in each. The benzol was carefully cooled, and a mixture of 600 grams of ordinary pure sulphuric acid and 120 grams of water slowly added to each flask, all heating being carefully avoided. Next, 100 grams of powdered MnO_2 were stirred into the mixture in each flask and the mixture then allowed to stand one week, with frequent stirring. The undecomposed benzol was then removed by distillation, the acid nearly neutralised with caustic soda and evaporated to a small volume, and this liquid treated with ether, which removed an organic acid from the liquid. This acid was then purified. It sublimed without decomposition, agreed

[1] Ann. d. Chem. **148**, 50.

in all physical properties with benzoic acid, and furnished barium and calcium salts, which, upon analysis, proved to be the benzoates of barium and calcium. The yield of benzoic acid is small. Carbonic anhydride was the other product of the oxidation which we observed. We were unable to convince ourselves of the presence of formic or phthalic acids.

We next examined the action of peroxide of lead and sulphuric acid upon benzol. By the action of these agents upon benzoic acid Meissner and Shepard[1] obtained succinic acid and carbonic anhydride. Benzol and PbO_2 were shaken together in a flask and sulphuric acid (sp. gr. 1.56) run in from a drop-funnel. Vigorous action accompanied by frothing takes place in the cold at first, afterwards gentle heating is required to complete the action. After 12 hours heating the undecomposed benzol was removed by distillation, the liquid diluted with water and filtered. The black residue consisted mostly of PbO_2 and $PbSO_4$ and contained no organic acid. The clear liquid was treated with $BaCO_3$ in excess, filtered and the filtrate evaporated to dryness. It furnished a barium salt soluble in water, containing 36.50 per cent. of barium and corresponding in every respect with benzoate of barium. The free acid from this salt showed all the physical properties of benzoic acid. The yield is much larger than by the action of MnO_2 and H_2SO_4 upon benzol. Carbonic anhydride is formed also in large quantities in the oxidation with PbO_2 and H_2SO_4.

The statements regarding the action of potassium permanganate upon benzol differ. Berthelot[2] obtained oxalic acid by the action of alkaline permanganate solution upon benzol, while Adrienz[3] found formic acid to be the product of the oxidation in an acid solution. The action is certainly very slow. A neutral solution of permanganate failed to attack benzol perceptibly in two weeks, as was proved by the weight of benzol recovered. A strongly acid solution in 12 days oxidised one-fourth of the benzol present, but we could not detect the production of solid or liquid products, while boiling with alkaline permanganate solution for six hours failed to oxidise any of the benzol.

We examined the action of PbO_2 and dilute nitric acid upon benzol. We boiled 50 grams of benzol, 104 grams of nitric acid (sp. gr. 1.4), 222 grams of water and 30 grams of lead peroxide

[1] Zeit. f. Chem. 1866, 752. [2] Compt. rend. **64**, 35.
[3] Berichte der deut. chem. Gesell. **6**, 443.

with a return cooler for 60 hours. After removal of the undecomposed benzol, the dilute acid deposited a crop of crystals which proved to consist of oxalic acid and no other oxidation product was observed. Leeds[1] obtained oxalic acid by the oxidation of benzol with ozone and with hydrogen peroxide.

By oxidising benzol with a solution of chromic acid in acetic acid and also by the action of potassium bichromate and sulphuric acid we obtained only carbonic anhydride.

II. *Action of Isobutyric Acid upon Aniline.*

Under my direction, Mr. F. L. Bardwell has examined the action of isobutyric acid upon aniline in the presence of zinc chloride. Kahlbaum's isobutyric acid was mixed with pure aniline in the proportion of one molecule of the acid to one molecule of aniline. The liquids were shaken together, but no evidence of chemical action could be detected; a small quantity of anhydrous zinc chloride was then added, whereupon the mixture at once turned to a mass of crystals, and a decided rise in the temperature of the mixture was observed. The crystals were easily soluble in water, and were decomposed by dilute caustic alkalis in the cold and aniline set free. The crystals were doubtless aniline isobutyrate. The crystalline mass obtained by the action described above was placed in a flask, melted, and boiled for from one to two hours beneath a return cooler. At the end of this time the flask was cooled, and contained then a solid mass of crystals. These crystals were washed with dilute hydrochloric acid to remove any undecomposed aniline. They proved to be somewhat soluble in cold water and easily soluble in hot water. Caustic alkalis did not attack them in the cold, but upon heating, decomposed them, furnishing aniline. The substance was crystallised repeatedly from water, and analysed when the melting point was constant, with the following results:

0.1535 gram of substance furnished 0.1130 gram of H_2O and 0.4165 gram of CO_2.

0.9110 gram furnished 68.14 cc. of N at 20° and 760 mm.

	Found.	Theory for isobutyranilide.
H	8.54 per cent.	7.97 per cent.
C	73.99	73.61
N	8.56	8.58

[1] Berichte der deut. chem. Gesell. **14**, 975.

These results show conclusively that the substance is isobutyranilide, isomeric with the butyranilide obtained by Gerhardt,[1] by the action of a mixture of butyric acid and butyryl chloride upon aniline. Isobutyranilide crystallises from water in colorless prisms which melt at 102.5° without decomposition. It distills also without decomposition. It is somewhat soluble in cold water, easily soluble in hot water, alcohol and ether. The yield of the anilide is increased by heating the mixture of aniline, isobutyric acid and zinc chloride in closed tubes at 150°. If aniline and anhydrous isobutyric acid are heated without zinc chloride in a similar manner, the anilide can be obtained, but only with difficulty and in small quantities.

Nitric acid acts with great violence upon isobutyranilide, and all attempts to isolate a nitro compound in a pure condition failed. By the action of bromine upon the anilide a monosubstitution product was obtained. The anilide was dissolved in cold water, and a current of air charged with bromine vapor passed through the solution. A heavy precipitate of a yellowish color separated. This substance was very insoluble in water, but readily soluble in hot dilute alcohol. It was purified by repeated treatment with animal charcoal in an alcohol solution, and repeated crystallisations from this solvent, and was finally obtained in colorless needle-shaped crystals.

A bromine estimation furnished the following figures: 0.1569 gram furnished 0.1220 gram of AgBr.

	Found.	Theory for $C_6H_4BrNHC_4H_7O$.
Br	33.15	33.05

The bromisobutyranilide melts at 128°, but can be sublimed undecomposed at a somewhat lower temperature. It is soluble in hot water and slightly in cold water, but could not be obtained from water in a crystalline form. It is easily soluble in alcohol. It is unaffected by cold caustic alkali, but hot caustic alkali dissolves it slowly without decomposition. By heating in a closed tube at 125° for several hours, with aqueous hydrochloric acid, it was decomposed and furnished the hydrochloride of parabromaniline. The free base obtained from this hydrochloric acid salt melted at 67°.[2] The compound obtained by the action of bromine upon isobutyranilide is therefore parabromisobutyranilide. The formation of an isomer was not observed. The parabromiso-

[1] Ann. d. Chem. 87, 166.

[2] Körner, Jahres. f. Chem. 1875, 356.

butyranilide was treated with a mixture of nitric acid and sulphuric acid, in the manner recommended by Nölting and Collin[1] for the production of nitracetanilide, and furnished a nitro compound difficult to purify, but which after repeated crystallisations from alcohol yielded a yellow crystalline product, melting at 111.5°, containing 36.37 per cent. of bromine, and agreeing in all respects with parabromorthonitraniline.[2]

III. *The Ethylorthotoluidines.*

In the course of an investigation upon the products of oxidation of the substituted aromatic amines, Mr. R. L. Chase has prepared under my direction the ethylorthotoluidines. These compounds were prepared by Reinhardt and Staedel,[3] but they furnished no description of their characteristics.

Ethylorthotoluidine.

Ethyl iodide combines with great readiness with orthotoluidine. If mixed in the proportion of 1 mol. of ethyl iodide to 1 mol. of orthotoluidine, and allowed to stand for twelve hours at the ordinary temperature, the mixture becomes a solid crystalline mass consisting of the hydriodide of ethylorthotoluidine. We dissolved this salt in water, in which it is very soluble, and added caustic potash solution, by which a base was set free as an oil. This oil dried over $CaCl_2$ and fractionated, furnished a product which boiled at 204°–206°, and gave the following figures upon analysis:

	Found.	Theory for ethylorthotoluidine.
C	79.52	80.00
H	10.03	9.63
N	10.34	10.37

Ethylorthotoluidine is a thin yellowish oil which gradually turns pink upon standing. Our product boiled at 204°–206°, and remained liquid at —15°. Its specific gravity is .9534 at 15.5° compared with water at the same temperature. Its platinum salt separates as an oil, and cannot be obtained in a state of purity owing to the ease with which it is decomposed. It resembles

[1] Berichte d. deut. chem. Gesell. **17**, 262.

[2] Hübner, Retschy, Berichte d. deut. chem. Gesell. **6**, 796, and Körner, Jahres. f. Chem. 1875, 328.

[3] Berichte d. deut. chem. Gesell. **16**, 29.

closely the corresponding salt of ethyl paratoluidine.[1] The hydrochloric acid salt of the base could not be isolated. The hydriodic acid salt separates from water as a jelly, but can be crystallised from alcohol, in which it is less soluble. An iodine estimation in the hydriodide thus purified gave 48.39 per cent. of iodine, while the theory requires 48.29 per cent. The acet-compound can be obtained either by the action of acetyl chloride or acetic anhydride upon the base. It is somewhat soluble in water, easily soluble in alcohol and benzol, and separates from these solvents as an oil. It boils between 254°–264°, and solidifies after long standing.

A nitrogen estimation in the acet-compound gave,

	Found.	Theory for acetethylorthotoluidine.
N	8.34 per cent.	7.91 per cent.

The ethylorthotoluidine furnishes by the method employed by Fischer[2] for preparing nitrosomethylaniline, a nitroso compound. This compound was purified by distillation with steam, and is a dark brown oil which cannot be distilled alone without decomposition. A nitrogen estimation gave,

	Found.	Theory for nitrosoethylorthotoluidine.
N	16.63	17.05

Diethylorthotoluidine.

When ethylorthotoluidine is heated with an excess of ethyl iodide at 100° for six hours in a closed tube the mixture turns to a mass of white crystals soluble in water. An aqueous solution of this salt treated with caustic potash solution yielded a free base, which was dried over $CaCl_2$, fractionated, and proved upon analysis to be diethylorthotoluidine.

	Found.	Theory for diethylorthotoluidine.
C	80.54	80.98
H	11.06	10.43
N	9.25–9.23	8.58

Diethylorthotoluidine appears to have been first prepared by Baeyer and Caro,[3] but is not described by them. Our product boiled between 203°–208°, and was a limpid oil, closely resembling the mono-compound. Its hydriodide is less soluble in water

[1] Morley and Abel, Ann. d. Chem. **93**, 311. [2] Ann. d. Chem. **190**, 151.
[3] Berichte d. deut. chem. Gesell. **10**, 1262.

than that of ethylorthotoluidine, and crystallises from it in beautiful prisms, which contain 1 mol. of water of crystallisation, and melt at 72°–73°. An iodine estimation in the anhydrous salt gave 43.78 per cent. of iodine, while the theory requires 43.64 per cent. The yield of diethylorthotoluidine was 70 per cent. of the theoretical quantity.

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THE OPTICAL PROPERTIES OF MALIC AND TARTARIC ACIDS.

BY LOUIS BELL.

Among optically active substances, these two acids have long been recognised as showing remarkable and inexplicable peculiarities. Much alike in chemical character, their optical properties are in most respects identical. Both show an increase of optical activity with a rise in temperature or with a decrease of concentration; both, in strong solution or at a low temperature, show a tendency to reverse the normal direction of optical rotation, and finally, under proper conditions, both actually reverse this direction, laevo-malic acid becoming dextro-rotatory, and dextro-tartaric acid becoming laevo-rotatory. Furthermore, each exists in a form itself optically inactive, but which may be split up into two forms, crystallographically enantiomorphous, and possessing optical activities sensibly equal and opposite.

This fact was shown for tartaric acid by the classical research of Pasteur,[1] while Bremer[2] extended it to malic acid. The optical properties correspond to the crystalline form so distinctly as to make it evident that the molecular structure which produces optical activity also induces crystalline asymmetry.

Both these acids also exhibit variable and anomalous rotary dispersion; tartaric acid in a very marked degree. In all respects their optical behavior is so nearly identical that facts established by investigation of the one will uniformly be true of the other.

[1] Ann. de Ch. et de Phys. (2) **24**, 442. [2] Ber. d. deut. chem. Ges. **13**, 351.

To explain some of these peculiarities, and, in particular, to assign a cause for the reversal of the direction of rotation, a phenomenon which implies some profound physical change, the following inquiries have been instituted.

The property of twisting the plane of polarisation is almost certainly due to some condition of asymmetry, either molar or molecular. In crystals it is always associated with enantiomorphs, in liquids it must be due to asymmetrical grouping or asymmetrical configuration of the molecule itself, while in gases it is quite certain that only the latter cause can operate.

In any case a change in the direction of this twisting is a change not of degree but of kind, and must involve an altered configuration of the material system upon which the ether waves impinge. In case of liquids, Le Bel[1] has shown optical activity to be associated quite constantly with the presence of an asymmetrical carbon atom.

In the consideration of malic and tartaric acids the increase of specific rotation on dilution calls for careful attention. It was first investigated by Biot in case of tartaric acid, but all that he could offer by way of explanation[2] was the extraordinary hypothesis that the acid impressed its optical properties on the whole mass of water with which it was mingled. In a problem essentially dynamical, this sort of explanation can have but little weight, and the solution must be sought elsewhere. It is evidently connected with the reversed rotation into which it gradually passes, and this in turn must plainly be associated with some change either in the molecules themselves or in their form of aggregation. Given a number of molecules twisting the plane of polarisation in a given direction, and there are four classes of causes which could reverse that direction. 1. Change of configuration of the molecule itself; 2. Formation of a hydrate or other chemical compound; 3. Building up of crystalline forms; 4. Formation of a polymeride rotary in the opposite sense from the free molecules. It is well to discuss these possibilities in order.

1. It does not seem probable that such a change could be produced by simple dilution, unaccompanied as it is by any marked thermal effects. Further, we know that the change can be produced, as when racemic acid is prepared from dextro-tartaric, but it is by no means readily effected. To form racemic acid in the

[1] Bull. Soc. Chim. **22**, 337. [2] Ann. de Ch. et de Phys. (3) **10**, 385.

way mentioned requires heating with water in sealed tubes for many hours to a temperature of 175°.[1] If such treatment is required to produce a laevo-rotatory modification of dextro-tartaric acid, it is highly improbable that it could be effected by any ordinary change in temperature or by any possible amount of dilution. And if the changes in temperature which produce such a marked effect on the optical activity do so by a change of configuration, *i. e.* from dextro to laevo forms, tartaric acid should crystallise in right or left handed hemihedral forms according to temperature. But such is not the case.

2. The hypothesis of a hydrate is at least quite plausible, and seems to have been the one tacitly adopted by many investigators. Biot in his later papers seems to have been inclined to accept it. The existence of a hydrate would explain most of the facts observed, and at first sight would appear very probable, but a close examination shows that no hydrate is formed.

In the first place hydrates are uniformly produced with evolution of heat, and in the case of one of the acids in question (racemic acid), the amount of heat given out has been accurately measured by Berthelot.[2] Hence we are justified in concluding that, if the dilution which so increases the specific rotation of tartaric acid is accompanied by the formation of a hydrate, it must also be accompanied by an evolution of heat. On the contrary, diluting a concentrated solution of tartaric acid causes a slight but unmistakable fall of temperature—the uniform sign of chemical decomposition or physical disintegration. This point was demonstrated in the following way: A small gas-washing bottle was fitted with a very sensitive thermometer passed through the rubber stopper which closed the lateral opening at the bottom. Enough distilled water to cover the bulb of the thermometer (usually 20 cc.) was then poured in, and the contraction in the cylinder was then closed by means of a rubber stopper fitted on the end of a glass rod. About 15 cc. of the solution to be tested was then placed in the upper part of the vessel, and the mouth was closed by a rubber stopper slipped over the rod before mentioned. Thus tightly closed the whole apparatus was immersed in water for some hours. Finally, without taking the vessel from the water or disturbing it in any way, the glass rod was slipped upward far enough to remove the stopper

[1] Jungfleisch, Bull. Soc. Chim. (2) **19**, 99.

[2] Comptes Rendus, **78**, 713.

from the contraction and allow the solution to run into the water. Solutions of tartaric and malic acids of from 20 to 40 per cent. were thus tested, and falls of temperature of from 0.1° to 0.2° were observed. The same is true of solutions of various salts, but the fact is none the less conclusive against the formation of hydrates of the above acids.

Again, since a hydrate is a definite chemical compound, after a hydrate was formed we should expect a condition of comparative stability to be reached, but in tartaric acid there appears to be no such definite compound completed.

Finally, the most characteristic of the optical properties of these acids, *i. e.* reversal of the direction of rotation by change in temperature, was discovered by Biot[1] in amorphous solid tartaric acid, in which case, from total absence of water, the possibility of a hydrate is obviously excluded. Biot had foreseen that a solution of tartaric acid would probably become laevo-rotatory if a sufficient degree of concentration could be reached, but had sought for the complete phenomenon in vain, till he found its analogue in the behavior of melted tartaric acid, which on cooling down passes, like the solution as it is concentrated, through decreasing rotations into a laevo-rotatory amorphous solid. I have recently succeeded in obtaining slight laevo-rotation from a concentrated solution in 95 per cent. alcohol at —15°.

Biot, throughout a most careful and exhaustive series of papers covering literally hundreds of pages of the Annales de Chimie et de Physique, was misled by the old formula of tartaric acid ($C_8H_8O_{10} + 2H_2O$) which represented it as containing water. Consequently he makes use of this hypothetical water even to explain the properties of the melted acid. His experiments, however, were very careful and elaborate, and his papers, scattered through the third series of the "Annales," cover most of the facts concerning rotary polarisation.

The hypothesis of a hydrate being thus excluded, the next possibility is the formation of crystal molecules. This hypothesis was suggested by Dubrunfaut, Erdman and Bechamp,[2] to account for birotation in milk sugar. For several reasons, however, it is not applicable to the present case. Whatever may be the nature of the modification which reverses the rotation in malic and tartaric

[1] Ann. de Ch. et de Ph. (3) **28**, 351.

[2] Jahresber. f. Chem. 1855, 671; 1856, 639.

acids, it certainly has a rotation direction opposed to that of the free acid. But malic acid shows little tendency to crystallise in any form whatever, and the crystals of tartaric acid correspond in optical character to the solution. Hence any structure that could fairly be called a crystal would not probably show any tendency to reverse the rotation. Further, the formation of crystals would necessitate a change in optical character more rapid than that observed, as will be shown later.

From the consideration of these facts it appears that while the observed facts can hardly be accounted for by the formation of true crystal molecules, a quite similar phenomenon—the formation of a polymeric modification—may prove to be a sufficient explanation.

Such a hypothesis, in the first place, explains and agrees with the phenomena observed. Consider the case of a solution of dextro-tartaric acid, or since the changes are here more rapid, of laevo-malic acid. As the concentration increases or the temperature falls, let a dextro-rotatory polymeride be formed. It is evident that the first effect would be to counteract the original rotation, and there must occur precisely what does occur in the acids in question, a lessening of the initial specific rotation by an increase in concentration or a fall in temperature.

Breaking up of this polymeride by dilution or heating would obviously reproduce the same series of phenomena in the reverse order.

Dissociation has been suggested as a possible cause of analogous optical properties by Oudemans,[1] but he refers it to the breaking up of a salt into its constituents, while in this case it seems to be true dissociation of a polymeride into its simpler and more stable form. Such polymerisation is quite comparable with that exhibited by aldehyde, cyanogen and some other substances, though from the ready solubility of the product the phenomenon is in this case by no means obvious. Oudemans also hints at the possibility of some molecular combination, but this is quite different from a polymeride possessing new and opposite optical properties.

Consider the conditions in such a solution. At any given concentration let m be the number of normal molecules and n the number of polymeric molecules, and let r and r' be their respective rotative powers. Then, evidently, the condition for reversal of rotation is

[1] Liebig's Annalen **166**, 73; **182**, 60.

that $nr' > mr$, where r and r' have opposite signs; while where $nr' < mr$ the normal rotation will be only decreased, and for $nr' = mr$ there will be no rotation. These conditions are general for any mixture of optically active substances.

For the case in question, since the molecule of one of the substances is composed of p molecules of the other, the additional condition is imposed that $np + m = A$, the total number of normal molecules before any formation of the polymer. Under these circumstances the condition for no rotation in terms of m will evidently be $m = \frac{Ar'}{rp + r'}$.

From this equation it appears that if r' were due to a crystalline form, in which p must be quite large, and were in magnitude fairly comparable to r, the change produced in the rotation would be large compared to the number of crystal molecules formed. Hence, when the change in rotation is gradual and extends over a wide range of temperature, there is reason to suppose that p is rather small.

Further, since the rotation is a function of the wave-length according to the formula $\alpha = \frac{B}{\lambda^2} + \frac{C}{\lambda^4}$,[1] all optically active substances must produce dispersion varying for each substance with the constants B and C, but varying in direction with the sign of α. Now if substances be mixed which give opposite signs for α, it is evident that a more or less perfect color compensation can be effected, according to the relative magnitudes of the constants. If these were equal, perfect achromatism would follow together with absence of rotation. If they were unequal, various sorts of irregular and anomalous dispersion must result; and when the rotation of the system is completely reversed, the dispersion will have changed its direction. If one of the substances is more affected by temperature than the other, the constants will vary and irregular dispersion must follow. Anomalous rotary dispersion is inexplicable unless the substance showing it be a mixture, for α is a function only of constants and powers of λ, and in rotary dispersion there is no analogue of absorption. Biot[2] has investigated experimentally this rotary dispersion, and found the partial achromatism, irregular dispersion and allied phenomena indicated above.

[1] Boltzmann, Pogg. Ann. Jubelband, S. 128. [2] Ann. de Ch. et de Phys. (3) **36**, 405.

Now these theoretical considerations are completely fulfilled by the properties of malic and tartaric acids. As a solution of malic acid becomes more and more concentrated the laevo-rotation gradually decreases, approaches the neutral point, and then, up to the limit of saturation, becomes more and more dextro-rotatory. For a temperature of 20° the neutral point is found in a solution containing 35.3 per cent. of the acid. A 70 per cent. solution has a specific rotation $[a]_D = +3.3°$.[1] The dextro-rotation of malic acid was first noticed by Arendtsen.[2] These phenomena are precisely what would follow the gradual formation of a polymeride; and if it is so formed, increase of temperature should break it up and restore the laevo-rotation. This actually happens;[3] and without knowledge of the fact, and proceeding on purely theoretical grounds, I found that a solution inactive at 20° could be made to pass from dextro- to laevo-rotation and back with the greatest ease. Further, it is to be noticed that the change of rotation produced by a given change in temperature grows rapidly less as the solutions used are more and more dilute, which phenomenon would be a natural consequence if a polymeride were gradually broken up by dilution, but is incomprehensible if the change is due only to rise of temperature.

In case of sodium malate, which in general shows a stronger tendency to laevo-rotation than the free acid, this phenomenon is far less marked; which seems to indicate that, there being a comparatively small amount of the polymeride formed, the change produced by its dissociation is correspondingly small. I have extended the observations given by Thomsen by measuring the change of rotation produced in a 10 per cent. solution of the acid by rising temperature. From 20° to 40° in a 100 mm. tube the change was less than 20′, from which it would appear that, in a very weak solution, the polymeride is almost completely broken up, and the change produced by heating would be little or nothing.

Tartaric acid is under all ordinary conditions dextro-rotatory, but becomes laevo-rotatory for blue rays in sulphuric acid solution,[4] and completely so for solutions in anhydrous ether, acetone, or alcohol at a low temperature (as previously mentioned). Its

[1] Schneider, Liebig's Annalen **207**, 262.
[2] Ann. de Ch. et de Ph. [3] **54**, 403.
[3] Th. Thomsen, Ber. d. deut. chem. Ges. **15**, 441.
[4] Biot, Ann. de Ch. et de Ph. (3) **10**, 385.

specific rotation, like that of malic acid, increases with the temperature.

But the most conclusive evidence that could be wished is furnished by its rotary dispersion. In a 10 per cent. solution the dispersion is normal, but, as the concentration is increased, anomalous dispersion appears, and passes through various phases, until in a 50 per cent. solution the rotation for the blue is less than for the red; and the gradual reversal of rotation goes on till, in a 90 per cent. solution, the blue is laevo-rotatory, and the dispersion is that normally belonging to a laevo substance. Furthermore, the same series of changes can be produced by changes in temperature, a 50 per cent. solution showing an entirely normal dispersion at 50°.[1] From these facts it is evident enough that tartaric acid undergoes modification into a laevo-rotatory form by concentration or lowering of temperature. It has been shown that this modification cannot be due to change of configuration or to a hydrate, while the only crystalline form of ordinary tartaric acid known has optical properties opposed to those which must be attributed to the above modification. The hypothesis of a polymeric modification explains the observed facts effectively, and renders the change of specific rotation by dilution comprehensible. For it is clear that a polymeride may be dissociated in this way, since Berthelot[2] has shown by a beautiful series of thermo-chemical experiments that racemic acid, which is well known to be a combination of dextro- and laevo-tartaric acid, is partially decomposed into its constituents by the simple act of solution. An analogous case of easy dissociation is furnished by nitrogen peroxide, N_2O_4, which is broken up very readily by heat.

Whether the polymeride thus found in tartaric (and malic) acid is a true chemical compound or a physical compound, it is not altogether easy to say, for the distinction is in general somewhat indefinite; but, since it is radically different from any known crystalline modification, and appears to be comparatively simple, the former view seems much the more probable. In solutions of other substances molecular aggregations certainly exist, as is shown by the thermal experiments previously mentioned, but do not exhibit any radical change of physical properties such as is here found.

The theory throws some light on the effect of solvents. One cannot fail to notice that these liquids in which tartaric acid is

[1] Krecke, Archives Néerlandaises **7**, 107. [2] Comptes Rendus **78**, 713.

difficultly soluble (acetone, etc.), are the ones which most diminish its rotation. In other words, those substances which do not facilitate dissociation by affording a ready solvent medium, allow molecular aggregations to produce the most marked effects. How far this may be able to account for the action of solvents on optically active substances in general remains yet to be seen. The same reasoning certainly holds for malic acid.

One other important fact must not remain unnoticed in the consideration of these acids. Each of them exists in more isomeric forms than can be accounted for by any theory yet advanced. Of tartaric acid there are the two active forms and two well-known inactive forms, while Staedel has shown[1] that the inactive tartaric acid obtained from glyoxal differs from the others. Even van't Hoff's hypothesis, usually so liberal with isomerides, accounts for but three forms (Die Lagerung der Atome im Raume, 37), and here are five.

With malic acid the case is much the same. There are two active forms, and probably three inactive forms, described by Bremer,[2] Pasteur[3] and Loydl.[4]

Racemic acid seems to be very closely related to the other inactive acids. Now, in racemic acid there is good reason to believe the molecule to be made up by a combination of right and left-handed molecules. If we consider how a dextro- and a laevo-form may be thus united and produce optical inactivity, it seems quite probable that they must be arranged with reference to a plane of symmetry. Considering now a body containing an asymmetrical carbon atom, and existing in dextro- and laevo-forms, the probability appears that such forms may be united each to each symmetrically to a plane, in four, and only four, different ways.

May it not be, that the unexplained isomerides of racemic acid, and the corresponding malic acid, which we believe to be combinations of right and left forms, differ from each other only in position with reference to their common plane of symmetry?

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[1] Ber. der deut. chem. Ges. **11**, 1752.
[2] Ber. d. deut. chem. Ges. **13**, 351.
[3] Ann. de Ch. et de Ph. (3) **34**, 46.
[4] Liebig's Annalen **192**, 80.

REVIEWS AND REPORTS.

Report on Analytical Chemistry.

A Method for the Quantitative Separation of Chlorine and Bromine.—E. Berglund.[1]

The method is based upon the fact that a mixture of acid sulphate and permanganate of potassium will liberate all of the bromine in a bromide, but cannot decompose a chloride; and that the bromine thus liberated can be completely removed from an aqueous solution by means of a rapid current of air.

The apparatus consists of the following parts: an absorption bulb containing dilute caustic soda (1 to 50); a small flask in which the mixture of chloride and bromide is placed; a small bottle for the dilute solution of permanganate (1 to 50); and a glass tube filled with cotton wool, through which the air necessary for the removal of the free bromine is filtered. The bottle for the permanganate and the flask in which the decomposition is effected are connected by means of a glass tube which extends to the bottom of each; so that by lowering or raising the bottle, air or permanganate, as may be desired, can be introduced into the decomposing flask.

The substance to be analysed is placed in the flask, dissolved in 50 cc. of water, and treated with 15 to 25 cc. of a solution of acid sulphate of potassium (1 to 10); an aspirator is then attached to the absorption bulb, and a quantity of the permanganate solution drawn over into the mixture of bromide, chloride and acid sulphate. The bottle containing the permanganate is then lowered, and air rapidly drawn through the apparatus ($\frac{1}{2}$ liter per minute) until all of the bromine has been transferred to the absorption bulb. The hypobromite formed during the absorption of the bromine is decomposed by ammonia. The excess of permanganate in the solution of the chloride is reduced by means of alcohol.

The quantity of material taken should not exceed one gram, and the bromine should be completely removed within one and one-half hours. If more than one gram is taken, the solution is too concentrated and some chlorine is liberated. It is not safe to dilute the larger quantity by adding more water, since the time required for the removal of the bromine depends upon the volume of the liquid from which it is to be removed; and if more than one and a half hours are consumed in removing the bromine, some of the chloride is decomposed.

[1] Zeitsch. für anal. Chemie **24**, 184.

If, owing to the minuteness of the quantity of bromide, it is necessary to work with more than a gram of the mixture, the substance is dissolved in 15 to 25 cc. of water, and treated in the manner already described. The absorption bulb will then contain all of the bromine and a little chlorine. But these can be perfectly separated by reducing the hypobromite by means of ammonia, neutralising with sulphuric acid, and then subjecting the solution to the same treatment as the original material.

If the quantity of chlorine is very small, the permanganate should be added in small portions, and after each addition the liberated bromine should be removed. In this case there is no danger that any of the chlorine will be carried over with the bromine. The method is especially adapted to the determination of small quantities of bromine in the presence of large quantities of chlorides; as, for instance, in sea water.

A New Method for Determining Nitrogen in Organic Compounds.—J. Kjeldahl.[1]

This method, which is applicable to all compounds except those which contain the nitrogen in an oxidised condition or in the form of cyanogen, depends upon the fact that when a nitrogenous substance is heated with strong sulphuric acid and then oxidised with permanganate of potassium, the whole of the nitrogen is converted into the sulphate of ammonium.

The details of the method are as follows: One gram of the substance is weighed into a flask having a capacity of about 100 cc. Ten cc. of concentrated sulphuric acid (free from ammonia) are added. The flask is then placed upon a wire gauze and the contents heated nearly to the boiling point. The substance chars and the liquid presents the appearance of tar, but if the heating is continued for 1 to 2 hours the acid liquid will again become almost colorless. When this stage has been reached, finely pulverised potassium permanganate is sprinkled into the flask. Owing to the violence of the oxidising action it is best to add small portions of the permanganate in rapid succession. When the solution has assumed a green color, sufficient permanganate has been added, and the contents of the flask are allowed to cool. By this treatment the nitrogen will have been completely converted into ammonium sulphate, and it will only be necessary to decompose it with caustic soda. For this purpose the acid liquid is transferred to a flask of about 750 cc. capacity. The flask is provided with a rubber stopper, having an outlet tube which inclines upwards and connects with a spiral condensing worm. The lower end of the condenser enters a small Erlenmeyer flask, containing a measured quantity of standard acid solution. About 40 cc. of a solution of sodium hydroxide, free from ammonia and of 1.3 specific gravity,

[1] Zeitsch. für anal. Chemie **22**, 366.

are added to the sulphuric acid solution, and the ammonia estimated in one of the usual ways.

The author analysed a large number and variety of compounds and obtained very excellent results.

The method is simple, accurate and expeditious. The author made fourteen determinations in a single day without assistance, and with sufficient apparatus the number could have been increased to twenty.

The Kjeldahl method for determining nitrogen in organic substances has been thoroughly tested and compared with the Varrentrapp-Will method by Heffter, Hollrung and Morgen.[1] The results obtained are highly satisfactory. The maximum limit of error in some 400 determinations made by the new method was .07 per cent. The method is fully as accurate as the soda-lime process, and possesses many advantages over the latter. These advantages are that it is much less expensive, and being much simpler in execution it permits of great economy in time. It is not necessary to have the substance to be analysed in a state of fine subdivision, and for liquid substances it is by far the most convenient. They have found it advantageous to treat 1 gram of the substance with 20 cc. of a mixture of 4 volumes concentrated sulphuric acid and 1 volume of fuming sulphuric acid. Two grams of phosphorus pentoxide are then added, and the operation carried on as recommended by Kjeldahl. They have also devised apparatus which facilitates the making of a large number of determinations simultaneously.

Petri and Lehmann[2] have found the new method of Kjeldahl to be admirably adapted to the determination of nitrogen in urine. 5 to 10 cc. of the urine, according to its concentration, are treated with 10 cc. of a mixture of concentrated sulphuric and fuming sulphuric acids, and subsequently oxidised with permanganate as directed by Kjeldahl. The authors publish the results of numerous analyses which establish the great accuracy of the method.

It is also strongly recommended by Bosshard.[3]

A Source of Error in the Determination of Nitrogen.

V. Meyer and Otto Stadler[4] found while making analyses of volatile organic sulphur compounds by the Dumas method that a considerable quantity of carbon monoxide collects with the nitrogen in the eudiometer. Especially is this the case when the combustion is rapid. The authors think it probable that the sulphur dioxide at first formed during the rapid combustion of organic substances rich in sulphur, reduces the carbon dioxide in the presence of the heated copper spirals. The carbon monoxide

[1] Zeitschrift für analytische Chemie **23**, 553. Chemiker Zeitung **8**, 432.
[2] Zeitschrift für physiologische Chemie **8**, 200. [3] Zeitsch. für anal. Chemie **24**, 199.
[4] Berichte der deutschen chemischen Gesell. **17**, 1576.

then passes over with the nitrogen, and the results obtained are therefore too high. By passing a mixture of sulphur dioxide and carbon dioxide over heated metallic copper, small quantities of carbon monoxide were obtained. It is therefore recommended in making determinations of nitrogen in volatile organic sulphur compounds by Dumas' method, to carry on the combustion very slowly, and to have a long layer of lead chromate in the front part of the combustion tube. The measured gas should also be tested for the presence of carbon monoxide.

On the Detection of Nitrogen in Organic Compounds.—C. Graebe.[1]

The author has found that the Lassaigne method for detecting nitrogen in organic compounds is not universally applicable. The method consists in heating the compound with metallic potassium, and then treating a solution of the cyanide thus formed with a mixture of ferrous and ferric compounds. The formation of Prussian blue indicates the presence of nitrogen in the compound tested. Graebe has found that the diazo-compounds in general do not give this reaction, and he thinks it probable that the nitrogen escapes as a gas before any cyanide is formed.

A Simple Method for the Quantitative Determination of Nitric Acid.—Wildt and Scheibe.[2]

The Tiemann-Schulze method for determining nitric acid has several sources of error, which may produce unreliable results. The nitric oxide, which is measured over water, is not entirely insoluble; and, unless the water has been previously boiled, it contains oxygen, which will convert a portion of the nitric oxide into nitric and nitrous acids. The consequence of these facts is that the method tends to give too low results. The authors have modified the process by passing the nitric oxide through a solution of sodium hydroxide, to remove all traces of hydrochloric acid from the gas, and then into a flask containing air and water. The nitric oxide is thus oxidised and dissolves in the water present. At the end of the operation the acid liquid is titrated with a standard alkali. The quantity of nitric acid is found at once, thereby avoiding the readings of temperature and barometric pressure as well as the calculations, which are necessary when the nitric oxide is measured.

Phosphorus. Method for Determining Phosphoric Acid Volumetrically.—O. von der Pforten.[3]

The phosphoric acid is precipitated with ammonium molybdate. The precipitate is thoroughly washed with an almost saturated solution of ammonium sulphate until all excess of ammonium

[1] Berichte der deutschen chem. Gesell. **17**, 1178.
[2] Zeitschrift für analytische Chemie **23**, 151.
[3] Zeitschrift für analytische Chemie **23**, 422.

molybdate has been removed. It is then dissolved in dilute ammonia, and the solution diluted to a definite volume. A measured portion, which should contain at least .3 gram MoO_3 and not exceed 30 cc. in volume, is taken for titration. 50 to 60 cc. of dilute hydrochloric acid and 8 to 10 grams of tin in sticks are added. The reduction is effected rapidly. The molybdenum present is reduced to the condition of suboxide, and the solution assumes a clear yellow color. The excess of tin is removed by filtration, and the solution then titrated with standard potassium permanganate. The suboxide is thus oxidised to sesquioxide, and from the quantity of permanganate used the quantity of molybdic acid present can be readily calculated. It was found that a constant relation exists between the proportions of phosphoric and molybdic acids present in the yellow ammonium phosphomolybdate, which is represented by 24 molecules of MoO_3 to one molecule of P_2O_5. The method gave good results, and is applicable in all cases in which phosphoric acid is separated by means of ammonium molybdate.

A New Method for the Qualitative Separation of Tin, Antimony and Arsenic.—E. Berglund.[1]

If a solution of the sulphides of tin, antimony and arsenic in sodium sulphide be boiled with copper oxide, the tin, antimony and arsenic will be converted into sodium stannate, sodium antimoniate and sodium arseniate, respectively. The copper oxide is best obtained by finely pulverising the granular oxide, which is prepared by igniting the nitrate. After treating the alkaline solution of tin, antimony and arsenic with copper oxide, the cuprous sulphide which is formed is removed by filtration, and to the filtrate ½ to ¾ its volume of alcohol is added.

If antimony is present it will be precipitated. In the filtrate from the antimony precipitate the alcohol is expelled by boiling, and ammonium chloride added in excess. A milk-white precipitate indicates the presence of tin. If only a little tin is present no precipitate will be formed. Into the solution, in which a precipitate may be suspended, sulphuretted hydrogen is passed until the precipitate is dissolved. If no precipitate was present, the sulphuretted hydrogen is passed into the solution for only a short time. The solution is then made alkaline with ammonia, and the arsenic precipitated with magnesia mixture. The ammonium magnesium arseniate is filtered off, and the tin in the filtrate precipitated by hydrochloric acid.

A New Reagent for Sodium, Ammonium and Lithium.—H. Hager.[2]

When sodium, ammonium, or lithium salts are treated with a solution of potassium stannosochloride, a white precipitate is pro-

[1] Berichte der deutsch. chem. Gesell. **17**, 95. [2] Pharm. Centralh. **25**, 289.

duced. The reagent is prepared by adding a solution of caustic potash, of 1.145 specific gravity, to a mixture of 5 parts of stannous chloride and 10 parts of distilled water until the solution has become almost perfectly clear. After allowing it to stand one hour, 5 parts of potassium hydroxide and 15 parts of distilled water are added. The reagent must be clear and colorless before it is used; and all excess of free acid, in the solution to be examined, must be neutralised with caustic potash. If compounds of the earths or metals are present, they must be removed by pure potassium carbonate before using the reagent. Boracic acid prevents the precipitation of sodium salts; but precipitation of lithium is not affected by it.

A New Method for the Separation of Copper and Cadmium.—P. Gucci.[1]

To the solution from which bismuth has been precipitated by excess of ammonia, and which still contains copper and cadmium, dilute hydrochloric, nitric or sulphuric acid is added until the hydroxides of both metals have been dissolved. A slight excess of a solution of ammonium benzoate (10 per cent.) is then added and the copper precipitated as copper benzoate. The cadmium may then be detected in the filtrate by means of ammonia and ammonium sulphide. When only a small excess of ammonium benzoate is added, the separation is so perfect that the method may be advantageously employed in quantitative analysis. The precipitated copper benzoate is collected upon a filter, and, after washing, it is dried and ignited in a crucible. The reduced copper is then oxidised with nitric acid and weighed as oxide.

Separation of Nickel and Cobalt.—Ilinski and Knorre.[2]

If a solution containing nickel and cobalt and free hydrochloric acid be treated with nitroso-β-naphthol, all the cobalt will be precipitated as cobalt nitroso-β-naphthol, while the nickel will remain in solution.

To the solution containing a mixture of nickel and cobalt sulphates or chlorides add a few cubic centimeters of hydrochloric acid. To the warm solution add a hot solution of nitroso-β-naphthol in 50 per cent. acetic acid and allow the precipitate to settle. When a further addition of nitrosonaphthol solution no longer produces a precipitate, the solution is filtered and the precipitate washed with a 12 per cent. solution of hydrochloric acid. To the dry precipitate a little pure crystallised oxalic acid is added. It is then ignited in a Rose's crucible in a current of hydrogen. The cobalt is weighed in the metallic state. In the filtrate the nickel is precipitated with potassium hydroxide, after the acetic acid has been removed by boiling, and finally weighed as metallic nickel.

H. N. M. and E. H. K.

[1] Berichte der deutschen chem. Gesellschaft **17**, 2659. [2] *Ibid.* **18**, 699.

THE MANUFACTURE OF "ACID" PHOSPHATES.

The manufacture of the so-called "Acid" Phosphates of commerce is generally considered to be rather a rule-of-thumb process. One is supposed to mix so much rock and acid and get such and such results. It is not often that even the chemist who is consulted by the manufacturer cares to enter largely into the details of the actual mixing. If he finds that the product does not come up to what the manufacturer desires, he generally contents himself with advising an increase of acid, or, what amounts to the same thing, a decrease of rock. If 80 per cent. of acid is not enough, 82 per cent. or 84 per cent. is recommended, and if that is not enough, then 86 per cent. or even 87½ per cent. But it is possible with ordinary Charleston Rock to calculate beforehand what the analysis should be. I say with ordinary Charleston Rock, for if the rock contains notable quantities of iron or aluminum the question is very much complicated. The ordinary Charleston Rock contains very small quantities of these troublesome substances, and for all practical purposes we may regard the phosphoric acid as existing in the form of tricalcium phosphate (bone phosphate). It certainly simplifies the question if we can assume that the initial reaction is the conversion of tricalcium phosphate into monocalcic phosphate and calcium sulphate by means of sulphuric acid.

I have undertaken some investigations into the nature of the phosphoric acid compounds formed immediately upon treating ordinary Charleston Rock with sulphuric acid. The rock was ground so that it entirely passed a 60° seive, it was then sampled, and submitted to a partial analysis, as only the moisture, silica, phosphoric acid, carbonic acid, iron, aluminum and lime were determined.

Two separate investigations were made, Nos. 1 and 2.

I.	Analysis of rock used.
Moisture,	6.52 per cent.
Insol. silica,	17.84
Sol. "	.10
Phosphoric acid,	22.82
Carbonic "	2.80
Peroxide of iron,	11.56
Oxide of aluminum,	.00
Lime,	33.60

The content here of iron is larger than usual.

Formula for making "acid" phosphate from this rock:

	lbs.
Rock,	1200
Sulphuric acid 47°B.	1050

Temperature of acid added 60° C. (140° F.), stirred 3 minutes.
Temperature in pan just before discharging 82° C. (180° F.)

Sample taken from pan just before discharging, put into bottle, closely corked, and cooled immediately. Analysed at once.

	Found.	Calculated.
Moisture,	27.75 per cent.	24.51 per cent.
Phos. acid sol. in water,	8.53	9.33
" " insol. in water,	2.92	2.84
" " sol. in. am. cit. 65°,	1.15	
" " insol. " " "	1.77	
" " total,	11.45	12.17

In regard to the method employed for calculating the analysis beforehand, it is simple and easily understood by any one possessing even a slight knowledge of the principles of chemical reactions. But at the outset a supposition has to be made which, although supported by evidence of great weight, still can not yet be taken as entirely authorised. This supposition is that the initial reaction goes on according to the formula:

$$Ca_3P_2O_8 + 2H_2SO_4 = CaH_4P_2O_8 + 2CaSO_4.$$

Assuming then that this is the reaction, let us see what follows therefrom. 100 lbs. of $Ca_3P_2O_8$ containing 45.81 lbs. P_2O_5 require 200 lbs. of H_2SO_4 of 53°B. (or *exactly* 53.1°B.) for complete decomposition into $CaH_4P_2O_8$ and $CaSO_4$. 200 lbs. 53°B. acid = 229 lbs. 47° B. The 100 lbs. $Ca_3P_2O_8$ contain 45.81 lbs. P_2O_5, so that to render soluble in water 1 lb. P_2O_5 there is needed 5 lbs. 47° B. acid, or 1 lb. 47° B. renders soluble .20 lb. P_2O_5. The rock used contained 22.82 per cent. P_2O_5; 1200 lbs. were used in the mixture, so that we have 273.84 lbs. P_2O_5 to render soluble. We require, therefore, 1369.20 lbs. 47° B. acid if we wish to make all of the phosphoric acid soluble in water. We actually used 1050 lbs. 48° B. acid, and as each pound of this renders soluble .20 lb. P_2O_5, we should have in the whole mixture of 2250 lbs. 210 lbs. P_2O_5 soluble in water, or 9.33 per cent.

As regards the P_2O_5 insoluble in water:

We should have used 1369.20 lbs. 47° B.; we actually used 1050 lbs., so that the difference between what we should have used and what we did use multiplied by the soluble-coefficient (if I may use the term), which in this case is .20, represents the P_2O_5 we might have made soluble, but did not $(1369.20 - 1050) \times .20 = 63.84$ lbs. P_2O_5 insoluble in water = 2.84 per cent.

It will be seen from a comparison of the "found" and "calculated" percentages that there is a difference of .80 per cent. between the two "solubles," and one of .72 per cent. between the two "totals," the excess in both cases being on the side of the "calculated." As regards the two "moistures," the excess in the "found" may be accounted for by some carbonic and hydrofluoric acids being driven off by drying, and counted hence as "moisture."

All things considered, the agreement between the "found" and the "calculated" is close enough for all practical purposes.

The better grades of Charleston Rock do not contain as much oxide of iron as this sample, and it is likely that it affects the P_2O_5 sol. in water, so that we might expect to find less "soluble" than is given by calculation.

Experiment No. 2 was conducted with a better rock than No. 1.

Experiment No. 2.

Analysis of rock used:

Moisture,	2.32 per cent.
Insol. silica,	11.56
Sol. "	.14
Phosphoric acid,	26.29
Carbonic "	3.33
Peroxide of iron,	3.35
Oxide of aluminum,	3.07
Lime,	38.55

Formula for mixing:

Rock (60 mesh)	1500 lbs.
Sulphuric acid 46° B.,	1200

Temperature of acid added 50° C. (122° F.), stirred 3 minutes.

Temperature in pan just before discharging 71° C. (160° F.)

Sample taken from pan just before discharging, put into bottle, closely corked, and cooled immediately. Analysed at once.

	Found.	Calculated.
Moisture,	22.45 per cent.	21.73 per cent.
Phos. acid sol. in water,	8.81	8.73
" " insol. in water,	5.01	5.87
" " sol. in am. cit. 65°	1.69	
" " insol. " " "	3.32	
" " total,	13.82	14.60

It will be remembered that both these analyses represent the acid phosphate at the very moment of discharging from the mixer. It is of the utmost importance to the manufacturer to ascertain what are the changes, if any, which take place in the article between the moment of mixing and the moment of selling. Let us suppose that 250-500 tons are made by formula No. 2 and dumped in a large pile, and let us further suppose that analysis No. 2 represents fairly the condition of the article when first made. What will the analysis be at the end of one week, or one month? It is impossible to say exactly what are the changes that go on, they are very complicated, and are determined by numerous conditions, no one of them clearly understood.

A lot of 250 tons made by formula No. 2, and with the same rock, gave, 3 days after mixing, the following analysis:

Moisture, ...	16.72 per cent.
Soluble phosphoric acid, . . .	9.34
Phosphoric acid insoluble in water,	5.69
" " soluble in am. cit. 65°,	3.52
" " insol. " " "	2.17
Total, ...	15.03

The temperature of the pile being 100° C. (212° F.) at the time of taking sample. As Wagner has remarked (in his Düngerfabrikation, p. 60), the composition of the superphosphate varies according to the composition of the crude phosphate used, the quantity of sulphuric acid employed, and very considerably according to the manufacturing process. There are so many things that influence the composition of the superphosphate, and the so-called "acid" phosphate, that to investigate them all requires much time and patience. It is sometimes surprising to see what a great difference in the product a small change in the formula can determine. The addition of 50 lbs. of water often causes variations not at all to be anticipated, while the humidity of the atmosphere is a point not to be overlooked. In another article I desire to discuss the chemical reactions that are begun and continued in the manufacturing and storing of "acid" phosphates. The old notion that the gain in "reverted" phosphoric acid is determined by the causes that affect the loss of "soluble" is not sustained by the facts in the case. (See my article on the "The Reversion of Phosphoric Acid in 'acid' and superphosphates made from Red Navassa Rock," Journ. Elisha Mitchell Soc. 1884, and Shepard and Robertson's recent admirable pamphlet on "The changes that occur in heaps of acid phosphate.") In the present state of knowledge it is hardly possible to say what those changes are.

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THE COMPOSITION AND EXAMINATION OF THE COMMERCIAL SULPHATE OF QUININE.[1]

The majority of chemists agree in representing the composition of the crystallised sulphate of quinine by the formula $(C_{20}H_{24}N_2O_2)_2 H_2SO_4 + 7H_2O$. But the commercial sulphate is never pure, it always contains sulphate of cinchonidine, as it is impossible to separate these sulphates by recrystallisation from water.

The ordinary examination consists merely in the estimation of the water, and the detection of the presence of the cinchonidine by

[1] Translated by W. R. Orndorff, from an article by W. F. Koppeschaar in the Recueil des Travaux chimiques **4**, 130.

means of the well-known reactions of Hesse and de Kerner, or by ether. Now since the value of the commercial article depends solely upon the quantity of quinine it contains, it is very desirable that this should be estimated. For this purpose three methods are available: first, that of Vrij, in which the quinine is determined in the form of sulphate of iodoquinine (herapathite). This method gives accurate results. The second consists in the separation of the alkaloids by means of ether. This has not given good results, because the two alkaloids combine with each other. The third and best method is the optical, which consists in practice in determining the specific rotatory power of a mixture of the tartrates by Oudemans' method.

Assuming a certain degree of concentration *A* as a standard, Oudemans found for the pure tartrate of quinine, $[\alpha]_D = -215°.8$, and for the pure tartrate of cinchonidine, $[\alpha]_D = -131°.3$. The author of this paper, adopting Oudemans' standard of concentration *A*, examined nine specimens of the commercial sulphate of quinine, and obtained specific rotatory powers varying from $-209°.84$ to $-203°.78$. A single sample gave him $-192°.42$. The quantity of tartrates obtained, after applying the correction for the part which remained dissolved, was from 95.77 to 91.86 per cent. The pure sulphate of quinine with seven molecules of water should give 93.58 per cent.

The composition of the nine specimens was therefore:

Sulph. of quinine, .	95.11	92.20	91.30	90.13	88.92	87.74	87.10	84.32	72.03
" " cinchonidine,	6.87	5.47	9.52	9.29	10.15	12.92	11.79	13.44	26.25
	101.98	97.67	100.82	99.42	99.07	100.66	98.89	97.76	98.28

According to Oudemans' experiments, the errors made in these estimations, using the Laurent polarimeter, are very small. The use of the tartrates also causes a slight error, which, however, has but little influence on the final result.

The author, having concluded from theoretical considerations that it was impossible to separate a mixture of the sulphates of quinine and of cinchonidine by repeated crystallisations from water, assured himself of the correctness of this conclusion by polarimetric experiments, which showed that though the quantity of cinchonidine became smaller it never entirely disappeared. It is only by preparing the acid sulphate, $C_{20}H_{24}N_2O_2$, H_2SO_4, $7H_2O$, or the hydrochloride, $C_{20}H_{24}N_2O_2$, HCl, $2H_2O$, that the two alkaloids can be separated. By afterwards transforming these salts into tartrates they can be shown by the polarimeter to be free from cinchonidine.

The tartrate and oxalate, like the normal sulphate, cannot be purified by recrystallisation from water. On account of this property the author points out that the two alkaloids are monacid. They give with bibasic acids double salts containing both alkaloids

at the same time, and these double salts differ in their properties from the simple salts.

While, according to Oudemans, the tartrate of quinine contains one molecule of water and that of cinchonidine two, the author finds from his own experiments that the double salt crystallises with one molecule of water. These experiments follow:

1. A mixture of air-dried tartrates, prepared from a commercial sulphate of quinine, gave at 17° C., concentration *A* (Oudemans),

$$[\alpha]_D = -205°.3,$$

from which the composition is calculated to be:

87.6 per cent. tartrate of quinine with one mol. of water,
12.4 " " " cinchonidine with two mol. of water.

The same tartrates lost 2.3 per cent. of water on heating to 125°–130° C. for eight hours in a paraffin bath. Assuming that these two tartrates were the ones with which we had to deal, the calculated loss would have been 2.5 per cent. water; while if we suppose that all the cinchonidine is in the form of the double salt and that this double salt contains only one molecule of water, the calculated loss would be 2.22 per cent., which is much nearer the quantity found.

2. A mixture of tartrates prepared in the same manner, but with another sample of sulphate of quinine, gave

$$[\alpha]_D = -206.°81,$$

from which the composition is calculated to be:

89.4 per cent. tartrate of quinine with one mol. of water,
10.6 " " " cinchonidine with two mol. of water.

The loss of water on heating was 2.21 per cent. Calculating on the first supposition it should be 2.46 per cent., on the second 2.219 per cent.

3. A mixture of tartrates prepared from a commercial sulphate of cinchonidine gave

$$[\alpha]_D = -140.°15,$$

from which we obtain:

10.46 per cent. tartrate of quinine with one mol. of water,
89.54 " " " cinchonidine with two mol. of water.

The loss of water was 4.09 per cent. Calculating on the first supposition it should be 4.374 per cent.; assuming that all the quinine is in the form of the double tartrate, 4.18 per cent.

As has already been stated, the author concludes from these results that the mixture of tartrates contains a double tartrate of quinine and cinchonidine, slightly soluble in water.

The accuracy of the polarimetric determination is greater if the specific rotatory power be calculated from the anhydrous salts. The specific rotatory power for the concentration *A* is then found

to be for the pure anhydrous tartrate of quinine $-220°.07$, and for the pure anhydrous tartrate of cinchonidine $-137°.67$, and the formula for calculating the quantity of anhydrous tartrate of quinine in one hundred parts,

$$220.07x + 137.67\ (100 - x) = 100\ [a]_D m.$$

But the influence of this correction upon the final result is very slight, as may be seen from the following cases:

A specimen of commercial sulphate of quinine gave 90 per cent. of air-dried tartrate, containing 2.3 per cent. of water; the 90 parts therefore contain 87.93 parts of anhydrous tartrate.

For the crystallised salt the specific rotatory power was

$$[a]_D = -205°.3,$$

and for the anhydrous salt,

$$[a]_D = -210°.13.$$

From the formula for the crystallised salt,

$$215.8x + 131.3\ (100 - x) = 100 \times 205.3,$$

we find that the crystallised tartrates are composed of:

87.6 per cent. tartrate of quinine with one mol. of water.
12.47 " " " cinchonidine with two mol. of water.

The 90 parts of crystallised tartrates therefore contain:

78.9 tartrate of quinine = 62.66 quinine = 84.32 sulphate of quinine;

11.1 tartrate of cinchonidine = 8.52 cinchonidine = 11.39 sulphate of cinchonidine.

From the formula for the anhydrous tartrates,

$$220.07x + 137.67\ (100 - x) = 100 \times 210.13,$$

we find:

87.9 per cent. anhydrous tartrate of quinine,
12.1 " " cinchonidine;

hence for the 87.93 parts:

77.29 tartrate of quinine = 62.76 quinine = 84.46 sulphate of quinine.

10.64 tartrate of cinchonidine = 8.49 cinchonidine = 11.16 sulphate of cinchonidine.

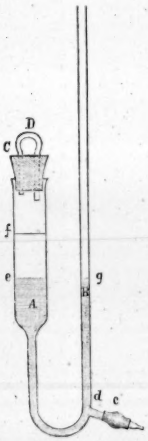
The difference of 0.1 in the quinine and 0.03 in the cinchonidine is not very great.

There has often been some uncertainty about the quantity of water of crystallisation of the normal sulphate of quinine, which is not the case with the acid sulphate nor the hydrochloride. The author thinks that the chemists who have estimated this water have used a sulphate of quinine containing some double sulphate of quinine and cinchonidine, and that this double sulphate contains

six molecules of water. In this case the pure sulphate of quinine crystallises with eight molecules of water, as Hesse assumes, and as is shown by Flückiger and Robiquet.

Method for Rapid Estimation of Urea.

Being called upon to make a good many brief and rapid analyses of urine on "clinic days" of our medical department, I devised the following modification of Knop's method of estimating urea, and after using it for a year with perfectly satisfactory results, venture to describe and recommend it as especially adapted for physicians' use, by reason of simplicity, cheapness and accuracy. In perfecting and testing it I was assisted greatly by J. Torrey, Jr., then working with me.



The apparatus consists of the glass tube *A*, which is about 8 cm. long and 2½ cm. in diameter, joined to the tube *B*, which is about 25 or 30 cm. in length in its longer arm and 8 or 10 in its shorter, and has a diameter of about 5 mm. Near the bend is an outlet tube *c*, provided with "ball valve" or pinch cock. *d*, *e*, *f*, *g*, are marks upon the tubes. *C* is a rubber cork with two holes through which the bent tube *D* passes. *D* is of such size and length as to hold about 1 cc., and one of its ends may be a trifle longer that the other.

The apparatus is used as follows: Remove the cork and pour in mercury until it stands at *e* and *g*, then fill up to the mark *f* with sodium or potassium hypobromite (made by shaking up bromine with a strong solution of sodium or potassium hydroxide). Next carefully fill the tube in the cork with the urine, being careful especially not to run it over or leave air bubbles in it. This can easily be done by using a small pipette, but if accidentally a little runs over it should be wiped off the end of the cork with blotting paper. The cork is then to be inserted closely into the tube, the urine tube being so small the urine will not run out in so doing. The mercury is then drawn out through *c* till it stands in *B* at *d*. Its level in *A* will of course not be changed greatly. Now, incline the apparatus till the surface of the hypobromite touches the urine in the longer part of the urine tube and then bring it upright again. The urine will thus be discharged into the hypobromite, which will of course decompose the urea, liberating nitrogen, which will cause the mercury to rise in *B*. Shake till no further change of level is seen, and mark the level of mercury in *B* with a rubber band, then remove the cork,

draw out the liquid with a pipette, dry out the tube above the mercury with scrap of blotting paper, pour back the mercury drawn out, and repeat the process to be sure that no error was made.

If now, two or three marks have been made upon the tube *B*, indicating the height of the mercury when solutions containing known per cents. of urea are used, an accurate opinion can be at once formed as to the condition of the urine as regards urea.

As is well known, normal urine contains about 2.5–3 per cent. of urea, so that graduations representing 2, 2.5, 3, and 4 per cents. are usually all that are needed, though of course many more can be easily made.

The results obtained with this apparatus have been repeatedly compared with those of more elaborate ones, and no practical difference observed. Evidently the same apparatus, differently graduated, might be employed to determine the carbonate present in such a substance as crude soda ash or other similar mixture. In such a case the weighed material would be put upon the mercury with water and the small tube filled with acid.

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Note on the Determination of Carbon Monoxide.[1]

It has been noticed by those who have used palladium chloride for the quantitative determination of carbon monoxide in gaseous mixtures (especially in air) where the proportion of CO is small, that the reaction takes place very slowly. Welitschkowsky,[2] for example, found that a series of from 3 to 5 Geissler bulbs was necessary for the complete absorption of the carbon monoxide and other reducing gases in mixtures of illuminating gas and air, and Fodor[3] found that air containing 1 volume of carbon monoxide in 1000 could not be safely passed through or over the absorbing solution more rapidly than at the rate of from 150 to 200 cc. per hour.

We have found that—since the gas must remain in contact with the solution for a certain length of time—additional security is gained by using mushroom-shaped flasks, which afford a large absorption surface, and by passing the gas in an intermittent stream. By the aid of an aspirator a partial vacuum is first established in the flask containing the palladium chloride; this is then filled with the gaseous mixture, and after the gas has remained in the first flask for 20 minutes, it is allowed to pass into a second and then into a third. All of the CO may be absorbed in the first flask, the others are added to afford security. This operation as described is a slow one, as much as 8 hours being

[1] Communicated by Prof. W. R. Nichols. [2] Archiv für Hygiene **1** (1883), 231.
[3] Vierteljahrsschrift für öffentliche Gesundheitspflege **12** (1880), 397.

sometimes required for a liter of air. We have found, however, that if the solution of palladium chloride is kept at a temperature of from 80° to 90° C., the reaction is complete at the end of 5 minutes, and a liter of air containing as much as 8 volumes of the monoxide in 1000, or as little as can be estimated at all, may be passed through a series of the smaller flasks in an hour and a half or through the larger flasks in half an hour. Working at this temperature we have experienced no difficulty from the formation of a basic salt.

The "mushroom-shaped flasks" are simply the show-glasses or show-bottles which are sometimes used in museums, especially for the display of seeds, etc. These are inverted and furnished with stoppers and conducting tubes; our larger ones have a diameter of about six inches, a depth (inside) of about an inch and a half in the center, and a capacity of about 375 cc.; the smaller ones have a capacity of about 100 cc.

It may be further noted that in titrating with potassium iodide it is essential that the solution of palladium chloride be made somewhat acid, as is clearly stated by Fodor. Welitschkowsky's statements as to the difficulties of the titration can be understood only on the supposition that this point was overlooked by him.

ELLEN H. RICHARDS.

On the Solubility of the Sulphides of Copper and Zinc in Melting Potassium Sulphide, and on their Insolubility in Melting Sodium Carbonate and Nitrate.

Some finely pulverised pyrites were melted in a covered porcelain crucible with an equal weight of potassium carbonate and half its weight of sulphur, the melted mass treated with hot water and the solution filtered. From this solution, when acidulated with hydrochloric acid, *all* the metallic substances dissolved were separated together with sulphur as sulphides in form of a brownish yellow precipitate, which, when after drying extracted with bisulphide of carbon, left a dark brown residue. This residue, melted with a mixture of sodium carbonate and nitrate, left, when extracted with water, a black powder soluble in hydrochloric acid, with green color. Sulphuretted hydrogen gave a precipitate with this solution; the brown deposit formed contained besides copper sulphide a small amount of lead sulphide, and the filtrate from it furnished, after addition of ammonia and ammonium sulphide, zinc sulphide. The solution separated from the black powder (see above) *did not contain any copper or zinc*, but traces of lead and small traces of arsenic. A quantitative determination of the above sulphides gave the following amount:

Copper sulphide	2.52	per cent.	of	the	quantity of pyrites taken.
Zinc	" 0.64	"	"	"	
Lead	" 0.0056	"	"	"	

EDO CLAASSEN.